

New Method to Quantitatively Determine the Spontaneity of the Emulsification Process

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A method to quantitatively determine the spontaneity (S) of the spontaneous emulsification process using a laser diffraction particle size analysis technique is presented. The method was experimentally tested by studying the rate of increase of the specific interfacial area ($\text{cm}^2 \text{mL}^{-1} \text{s}^{-1}$) and the equilibrium specific interfacial area for different systems formed by the surfactant Brij30 dissolved in linear alkyl oils ($\text{C}_8\text{--C}_{16}$) when brought in contact with ultrapure water. The experimental results confirmed the effectiveness of the proposed method, and they also suggest that the oil chain length of the linear alkyl oils has an important effect on the driving force of the spontaneous emulsification process in these systems. Finally, a molecular spontaneous emulsification mechanism is proposed for the systems studied.

Introduction

Spontaneous emulsification is a phenomenon that occurs when two immiscible liquids are placed in contact with each other and emulsify *without* the aid of any external thermal or mechanical energy source. Depending on the liquids involved, the presence of appropriate surfactants, pH, or other imposed electrical potentials, it may take from a few minutes to several days for completion of the spontaneous emulsification process.¹ This phenomenon of spontaneous emulsification is also achieved by inversion of the coexisting liquid phases; that is, the external phase becomes the internal one, and vice versa, through a phase transition driven by different factors such as temperature or concentration changes^{2–5} or through an osmotic pressure gradient.⁶ Spontaneous emulsification can be important in the design of emulsions having (a) a small drop size distribution (even of the order of nanoemulsions),^{2–6} (b) a highly concentrated internal phase, and/or (c) low energy consumption.^{3–6} This phenomenon has found a variety of industrial applications such as self-emulsifying drug delivery systems (SEDDS)⁷ and agricultural sprays and pesticides.^{8,9} It also has

potential applications in enhanced oil recovery (EOR)^{8,10,11} and detergency.^{12,13}

In practice, one only observes the rapid formation of cloudy dispersions; it is difficult to measure the kinetics of spontaneous emulsification. However, recent advances in video imaging and laser and light scattering techniques for size distribution of droplets have made it possible to measure the rate of spontaneous emulsification. The technique currently used in industry to measure the spontaneity of an emulsification process is known as the Collaborative Pesticide Analytical Committee of Europe test, commonly referred to as the CPAC test.⁹

CPAC Test. In this technique, a 1 mL bulb pipet is vertically supported with the tip about 4 cm above the surface of water at the 100 mL graduation mark in a 100 mL graduated cylinder.^{9,14} The oil content in the bulb is allowed to fall freely into the water, and the ease of emulsion formation is visually evaluated and expressed in a qualitative fashion as *good*, *moderate*, or *bad*. This method presents serious disadvantages such as the following: (a) the data obtained cannot be meaningfully compared with data obtained in other laboratories, since this technique relies on visual appreciation; (b) most oils are lighter than water, that is, only a few oil layers will be in contact with fresh water, thus slowing down the emulsification rate; and (c) the rate at which the oil will disperse down into the water phase strongly depends on the difference in density between the oil and water. However, the CPAC test has been widely used despite its poor interlaboratory reproducibility, mainly because of its ease of application and because it does not require the use of sophisticated instrumentation.^{9,14}

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[‡] Department of Chemical Engineering.

(1) Davies, J. T.; Rideal, E. K. In *Interfacial Phenomena*; Academic: New York, 1961.

(2) Forgiarini, A.; Esquena, J.; González, C.; Solans, C. *Langmuir* **2001**, *17*, 2076.

(3) Forgiarini, A.; Esquena, J.; González, C.; Solans, C. *Prog. Colloid Polym. Sci.* **2000**, *115*, 36–39.

(4) Kunieda, H.; Fukui, Y.; Uchiyama, H.; Solans, C. *Langmuir* **1996**, *12*, 2136.

(5) Ozawa, K.; Solans, C.; Kunieda, H. *J. Colloid Interface Sci.* **1997**, *188*, 275.

(6) Greiner, R. W.; Evans, D. F. *Langmuir* **1990**, *6*, 1793.

(7) Wakerly, M. G.; Pouton, C. W.; Meakin, B. J.; Morton, F. S. *Phenomena in mixed surfactant systems*; ACS Symposium Series Vol. 311; American Chemical Society: Washington, DC, 1986; p 242 and references therein.

(8) Groves, M. J. *Chem. Ind.* **1978**, *12*, 417 and references therein.

(9) Becher, D. Z. In *Encyclopedia Of Emulsion Technology*; Marcel Dekker: New York, 1983.

(10) Rivas, H.; Gutierrez, X.; Zirrit, J. L.; Antón, R. E.; Salager, J. L. In *Industrial Applications of Microemulsions*; Marcel Dekker: New York, 1997.

(11) Pillai, V.; Kanicky, J. R.; Shah, D. O. In *Handbook of Microemulsion Science and Technology*; Marcel Dekker: New York, 1999.

(12) Raney, K. H.; Benton, W. J.; Miller, C. A. *J. Colloid Interface Sci.* **1987**, *117* (1), 282.

(13) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1989.

(14) Groves, M. J.; Mustafa R. M. A. *J. Pharm. Pharmacol.* **1974**, *26*, 671.

Turbidity Test. As suggested by Groves and Mustafa,¹⁴ it is possible that information on the time needed to reach the equilibrium point might be obtained by injecting a fixed volume of oil into a flowing stream of water and taking measurements downstream of the mixing point; that is, the degree of “spontaneity” is expressed as a characteristic time. This method reports the time required to reach a constant value of average drop size as an indicative parameter of emulsion spontaneity. The *turbidity of a system* that undergoes self-emulsification is monitored over time until it reaches a constant average value. In the emulsion formation process, the mean drop size decreases while the total number of drops increases. It was assumed by Groves and Mustafa¹⁴ that these processes continue until the equilibrium conditions between disruption and coalescence processes are reached. At this point, the particle size distribution, and possibly the overall turbidity of the system, will remain nearly constant. Therefore, emulsification spontaneity is characterized as the time required to reach the equilibrium conditions where the average drop size does not change. This method has a major drawback, namely, that even though the time to reach equilibrium is a good characterization of the kinetics of emulsification spontaneity, it nevertheless does not provide information on the extent of the emulsification process (i.e., the amount of interfacial area created). Finally, Groves and Mustafa¹⁴ made a comparative analysis of their method with the CPAC test and found that there is a close correlation between the two techniques.¹⁴

Specific Interfacial Area Test (SIAT). In the present work, it is proposed that the spontaneity of an emulsification process should account not only for the rate of emulsification but also for the volume fraction of the final internal phase as well as for the drop size distribution of the produced emulsion (or the total expanded interfacial area). The present work provides a simple approach to assess the spontaneity of some systems in a quantitative way. The proposed method assumes that emulsification is an energy-driven process which is directly related to the formation of the new interfacial area. The interfacial free energy increases as the interfacial area grows due to the breakage of drops into smaller droplets, and the dispersed volume remains constant. In the case of a spontaneous process, the required interfacial free energy is provided by the excess internal energy of the system upon mixing of the two liquids. Consequently, the spontaneity is directly related to the amount of free energy of the system. The minimum energy (ΔG_{int}) required to create new interfacial area is then given by the integral of the interfacial tension (γ) with respect to the increase in interfacial area (dA), namely,

$$\Delta G_{\text{int}} = \int \gamma dA \quad (1)$$

where both γ and A are time-dependent parameters.

To test the proposed method, Brij30 was dissolved in several linear alkyl oils (specifically, C_8 – C_{16}). The Brij30/linear alkyl oil/water systems were chosen because, according to Forgiarini and Solans,^{2–3} they show formation of nanoemulsions with low energy consumption, suggesting the possibility of the presence of a spontaneous emulsification phenomenon. Shah et al.¹⁵ probed this system and found that its spontaneous emulsification process seems to follow several mechanisms. Figure 1 schematically represents the phase diagram of the Brij30/

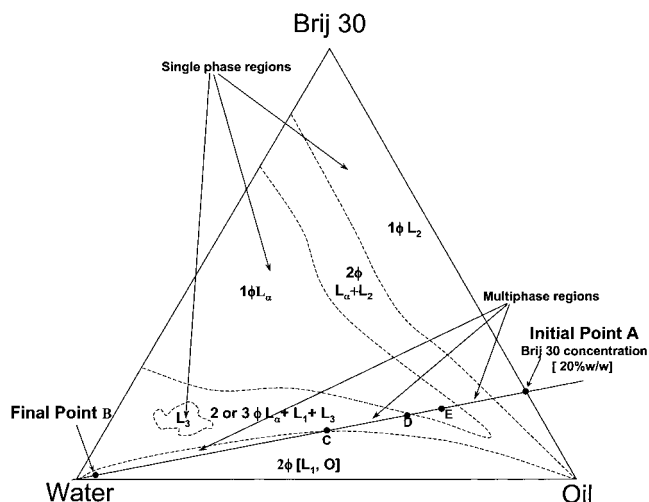


Figure 1. Schematic of the phase diagram that corresponds to all the Brij30/alkyl oil/water systems studied. The dashed straight line connecting points A and B represents the spontaneous emulsification process protocol. Point A corresponds to the initial concentration, and point B is the final concentration reached when the spontaneous emulsification process is over; these points correspond to points A and B in Figure 2. O, oil phase; W, water; L_1 , oil-in-water (O/W) microemulsion; L_2 , water-in-oil (W/O) microemulsion; L_3 , sponge phase; L_α , lamellar liquid crystal phase; A–E, specific composition points of the systems in the phase diagram; ϕ , phase.

oil/water system and the transition phase that takes place as the Brij30–oil system evolves from its initial concentration (point A) to the final concentration reached when the spontaneous process due to the mixing with water is complete (point B). Phase diagrams for the systems water/Brij30/decane and water/Brij30/hexadecane have been developed by Solans et al.^{2,16} The diagrams present striking similarities, and the assumption is made that the rest of the systems used in this work follow an analogous pattern.

Experimental Section

Materials. The surfactant Brij30 (polytetraoxyethylene dodecyl ether) was purchased from Sigma-Aldrich Co. The oil phase was composed of linear alkyl oils (C_8 – C_{16}) purchased from Fisher Scientific. Distilled water was obtained from a Milli-Q-Plus water filtration system.

Instruments. The drop size distribution experiments were carried out in a laser diffraction particle size analyzer (Coulter Counter Sizer LS 230) with the help of micropipets of 0.5–10 μL . All the systems were prepared using a balance (Sartorius, model BP211D) with 5 figures of precision.

Methods. Determination of Droplet Size and Increase in Interfacial Area. Solutions of Brij30 and linear alkyl oils of various chain lengths were prepared at 20% w/w concentration of surfactant. A 10 μL sample of the prepared solution was added with a micropipet into the main chamber of the Coulter Counter Sizer, which was gently stirred at 480 rpm throughout the entire process. The stirring speed was sufficient to keep the emulsion well stirred. The chamber was kept filled to its maximum capacity of 125 mL with ultrapure water. After 90 s of operation and for certain time intervals set by the operator, the instrument reports statistical information, such as the specific interfacial area (S) and mean drop radius (R). It also provides the corresponding curves for the drop size distributions of the emulsions spontaneously formed in the process. All this statistical analysis is given by the Beckman Coulter software with the exception of the initial specific interfacial area (S_0), which nevertheless can be calculated as the area of a sphere with the initial radius $R_0 = 0.13$ cm, since

(15) López-Montilla, J. C.; Herrera-Morales, P. E.; Shah, D. O. To be published.

(16) Personal communication with Dr. Conxita Solans and Dr. Anna Forgiarini at Departament Tecnologia de Tensioactius, Institut de Investigacions Químiques y Ambientales de Barcelona, CSIC. Spain. Universitat de Barcelona.

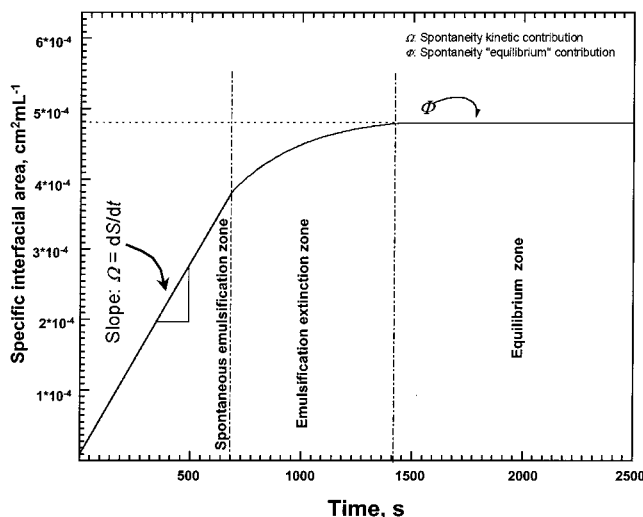


Figure 2. Schematic of the expected change of specific interfacial area with time; this is directly related to the quantitative measurement of the spontaneity. Zone 1 corresponds to the spontaneity kinetic parameter (Ω), i.e., the slope of the straight line. Zone 2 corresponds to an immediate region where the spontaneous emulsification process finishes due to energetic constraints. Zone 3 represents the equilibrium condition reached by the system once the spontaneous emulsification is over. This is directly related to the extension of the emulsification process.

this is the minimum area that corresponds to a volume of 10 μL . The calculation is performed according to the formula

$$S_0 = \frac{4\pi R_0^2}{\left(\frac{4\pi R_0^3}{3}\right)} = \frac{3}{R_0} \quad (2)$$

where R_0 is the radius of the initial drop. For this experimental setup, $S_0 = 23.08 \text{ cm}^2/\text{mL}$, which represents the initial area per unit volume of dispersed phase.

The experimental procedure was repeated for different samples in order to characterize thoroughly the change in drop size and the increase of the interfacial area with respect to time. After each run, the chamber was cleaned using a standard protocol. First, the emulsion is completely drained while ultrapure water is kept running constantly throughout the chamber. Second, once the chamber is empty, it is filled once again with ultrapure water and left for 1 min with the system running. This step is performed twice. Finally, the chamber is filled a third time with ultrapure water and is ready for a new experiment.

Results and Discussion

The hypothesis furthered in this work is that one should be able to indirectly measure the spontaneity of the process by measuring the variations in specific interfacial area with time. The proposed method (sketched in Figure 2) consists of determining the two factors contributing to emulsification spontaneity \mathbf{S} : (1) the kinetic parameter (Ω), which is the initial rate of change of the specific interfacial area, and (2) the equilibrium parameter (F), which is the final specific interfacial area. This can be expressed as a vector.

$$\mathbf{S} = \begin{pmatrix} \Omega \\ \Phi \end{pmatrix} \quad (3)$$

where \mathbf{S} is the spontaneity vector. Note that

$$\Omega = \left. \frac{dS}{dt} \right|_{t=0} = \left. \frac{1}{V} \frac{dA}{dt} \right|_{t=0} \quad (4)$$

and

$$\Phi = \lim_{t \rightarrow \infty} S(t) \quad (5)$$

where t is time, A is the total interfacial area, V is the total volume of the dispersed phase, and S is the specific interfacial area defined as $S = A/V$.

The schematic of the expected increase in specific interfacial area with time for spontaneous emulsifying systems shown in Figure 2 has three time zones, as follows:

(1) Spontaneous Emulsification Zone. Here the large drops massively split into droplets quickly increasing the specific interfacial area due to the large initial amount of excess internal energy available for this process. This region presents an almost linear behavior, whose slope defines the spontaneity kinetic parameter (Ω).

(2) Emulsification Extinction Zone. At this point, the spontaneous emulsification process starts to slow because the initial driving force decreases as the chemical potential of the surfactant in the various phases approaches an equilibrium condition.

(3) Equilibrium Zone. This region corresponds to the final condition reached by the system, once the spontaneous emulsification process is over. This final value of the specific interfacial area stands for the equilibrium parameter to the spontaneity (F).

Figure 3a shows the differential drop size distributions of the Brij30/ C_{12} /water system for three different times, starting at 90 s after the oil phase is brought in contact with water. At initial times, three different modes are clearly distinguished. It is believed that mode I and mode II are generated as a consequence of the spontaneous emulsification process, while mode III is generated by mechanical forces present in the system due to the stirring. Mode I corresponds to the formation of small droplets due to a high concentration of surfactant molecules at the oil-water interface. These surfactant molecules, under appropriate physicochemical conditions, massively partition into the aqueous phase dragging some oil molecules with them. Simultaneously, there is a formation of drops with a mean diameter in the order of 5 μm (mode II). Mode III corresponds to large drops (100 μm) which are produced by the mechanical energy of the stirring process. These large drops eventually disappear when they spontaneously emulsify as time approaches 1000 s. The experiments were run several times for the same system (i.e., same alkyl oil in the oil phase), and there was no significant variation in the results.

In Figure 3b, the effect of the oil chain length on the volume-weighted droplet size distribution for three different Brij30/alkyl oil/water systems at 90 s is shown. As with the time, this distribution strongly depends on the oil chain length. Because of this effect, the distribution may present one or several of the modes. It was observed that all the systems studied in the present work emulsify spontaneously.^{2,3,15} The formation of drops with a mean diameter in the order of 5 μm was a common occurrence among all the systems (mode II in Figure 3b). Since this is the only common feature in the drop size distributions, it is believed that mode II is a direct consequence of the spontaneous emulsification process that takes place in every system. Systems with longer oil chain lengths present a mode corresponding to a droplet size around 100–300 nm (mode I). It is very important to stress the fact that such submicron-size droplets cannot be formed by mechanical means, since the mechanical energy required under the present experimental conditions to achieve these drop sizes would be enormous. The genera-

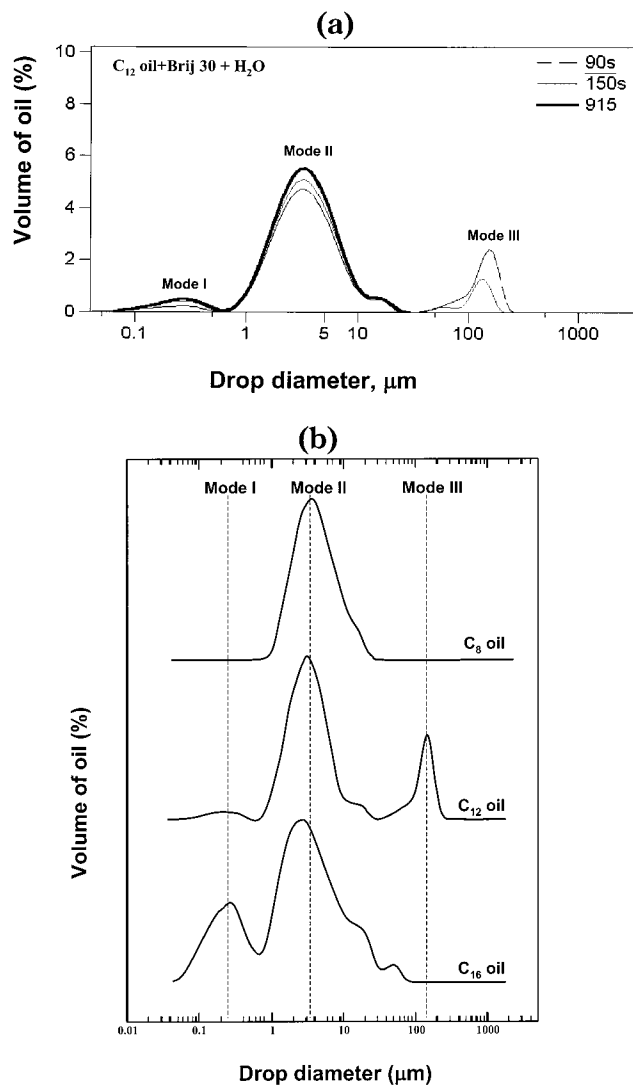


Figure 3. (a) Differential droplet size distributions of the Brij30/ C_{12} /water system for three different times. The volume-weighted distribution indicates how much oil was emulsified with each particular drop size. (b) Effect of the oil chain length on the volume-weighted drop size distribution for various Brij30/alkyl oil/water systems at 90 seconds. C_8 oil, C_{12} oil, and C_{16} oil refer to the systems Brij30/*n*-octane/water 20% w/w surfactant, Brij30/*n*-dodecane/water 20% w/w, and Brij30/*n*-hexadecane/water 20% w/w, respectively.

tion of extremely small submicron-size droplets (mode I) provides additional evidence of spontaneous emulsification. The formation of these submicron droplets appears to be due to the migration or transfer of surfactant molecules from the oil to the water phase. This very small drop size has a dramatic contribution to the increase of the specific interfacial area. Oils with long oil chain length present a third mode of drop size around 50–300 μm (mode III), which might correspond to mechanical effects.

The drop size corresponding to mode II (diameter = 3–5 μm) is in good agreement with experimental observations of the same systems made by Shah et al. using enhanced videomicroscopy.¹⁵ Shah et al. observed that the systems studied here present a strong interfacial instability and formation of a liquid crystal phase. They also note that when a drop of oil is brought in contact with water, the oil drop splits into tiny droplets.¹⁵ Therefore, the formation of mode II in the distributions presented in Figure 3b is driven by a combination of low interfacial tension and interfacial instability (e.g., interfacial tur-

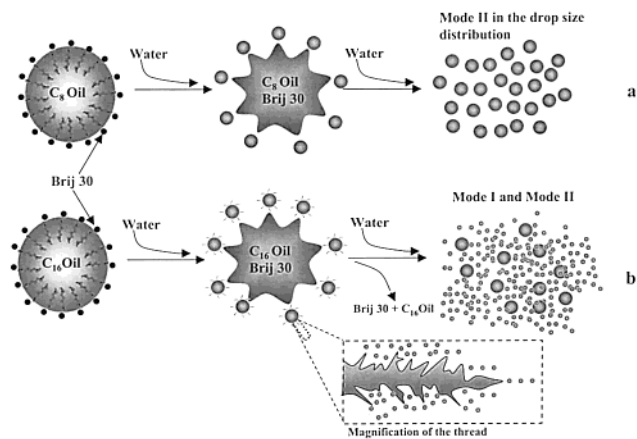


Figure 4. Schematic representation of the proposed spontaneous emulsification mechanism for the system Brij30/alkyl oil when brought in contact with water: (a) Brij30/*n*-octane 20% w/w; (b) Brij30/*n*-hexadecane 20% w/w.

bulence). In particular, the process of spontaneous emulsification for systems with small oil chain lengths (e.g., C_8 oil in Figure 3b) presents only mode II. In this case, the affinity of Brij30 for the oil phase is higher than in those for oils with longer oil chain lengths.^{17–20} Consequently, surfactant molecules crowd the interface in short chain length oils, for example, C_8 oil, but will not migrate in appreciable extent into the aqueous phase inducing low interfacial tension and strong interfacial turbulence breaking the oil drop into micron-size droplets. With an increase in the oil chain length (C_{12} and C_{16} in Figure 3b), the affinity of the surfactant for the oil phase decreases^{17–20} inducing an additional driving force for the emulsification process (resulting from the migration of the surfactant molecules into the aqueous phase dragging some oil molecules with them). This additional driving force is then able to produce submicron-size droplets (mode I for C_{12} oil and C_{16} oil in Figure 3b). Mode III that appears for systems with large oil chain length (C_{12} and C_{16} in Figure 3b) is probably a result of mechanical forces due to the stirring process. The contribution of mode III to the increase in the specific interfacial area is negligible. Figure 4 schematically illustrates the molecular mechanism proposed above for the observed results on spontaneous emulsification for C_8 and C_{16} oils.

The effect of the oil chain length on the final specific interfacial area (F) and its rate of increase as a function of time (O) for different Brij30/alkyl oil/water systems is presented in Figures 5 and 6. Figure 5 presents the trend of the expansion of the specific interfacial area as a function of time and is in good agreement with the schematic outlined in Figure 2 for the expected spontaneity behavior. Although the majority of the systems studied lie on the expected trend, the behavior of the systems containing pentadecane and hexadecane is different from the rest. Systems with pentadecane are characterized by a slow decay of the rate of increase of the interfacial area, whereas systems containing hexadecane present very large values of both O and F . Figure 6a presents the slope of the initial portion of the curves shown in Figure 5 (i.e., the spontaneity kinetic parameter) versus the oil chain length.

(17) Kunieda, H.; Solans, C. In *Industrial applications of microemulsions*; Marcel Dekker: New York, 1997.

(18) Nakajima, H. In *Industrial applications of microemulsions*; Marcel Dekker: New York, 1997.

(19) Chan, K. S. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1978.

(20) Shah, D. O. In *Proceedings of the European Symposium on Enhanced Oil Recovery*; Elsevier: Lausanne, 1981.

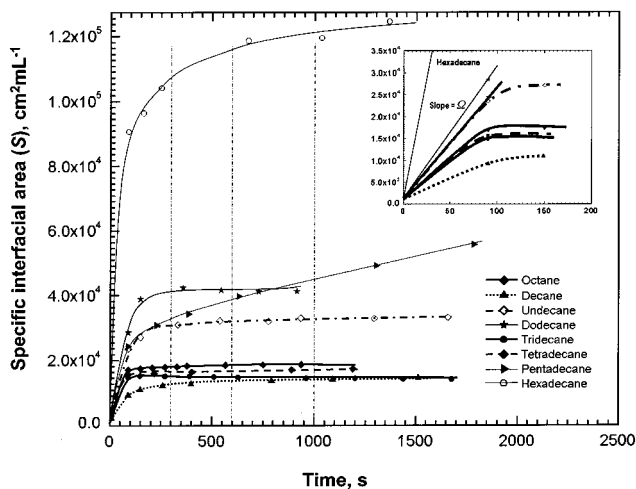


Figure 5. Experimental results for the change of the specific interfacial area with time for various Brij30/oil/water systems. The inset at the upper right corner is a magnification of the left bottom corner of this plot, and it is shown to clarify the fact that the slopes are calculated making the assumption that the emulsification process follows a straight line up to a time of 90 s.

Originally, it was hypothesized that since Brij30 has 12 carbon atoms in its oil chain, it is similar to the structure of dodecane (C_{12}), and consequently this would produce a lower interfacial tension than that of other oils due to a chain length compatibility effect.^{17–20} The experimental results, however, not only present the expected maximum for C_{12} but also show an unexpected large increase of the spontaneity kinetic parameter for long oil chain lengths (C_{15} and C_{16}). It is thought that the increase in the oil chain length makes it more difficult for Brij30 to partition into the oil phase when exposed to water. Figure 6b presents the effect of the oil chain length on the spontaneity equilibrium parameter for several times. The similarity of this figure with Figure 6a suggests that the kinetic parameter affecting the spontaneity in the systems studied here is proportional to both the spontaneity kinetic and equilibrium parameters.

Conclusions

The proposed method is an effective approach to quantitatively measure the spontaneity of the spontaneous emulsification process of the systems analyzed in the present work (see Figures 5 and 6).

The spontaneous emulsification process causes the volume-weighted drop size distribution to vary with time toward a distribution with lower droplet diameters (see Figure 3a). The oil chain length also has an important effect on the volume-weighted drop size distribution, which in turn dramatically affects the specific interfacial area expansion, that is, on the spontaneity (see Figure 3b).

The spontaneous emulsification of the Brij30/linear alkyl oil systems put in contact with water produces a multimodal volume-weighted drop size distribution. Drops corresponding to mode I and mode II (see Figure 3a,b) are produced by two different spontaneous emulsification mechanisms (see Figure 4). The formation of droplets corresponding to mode II (the only common mode of the drop size distributions for the different systems) is due to a combination of several spontaneous emulsification mechanisms regardless of the oil chain length (i.e., this mode is present in the distribution of any of the systems studied). On the other hand, the affinity of the Brij30 for the oil and water phases is the factor determining the formation of submicron-size droplets (mode I).

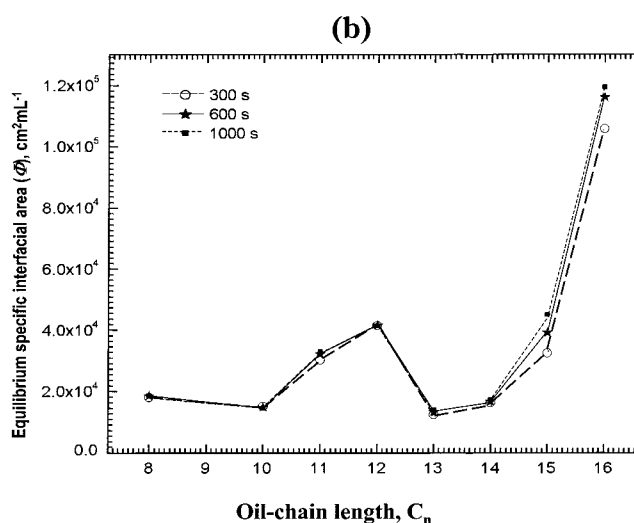
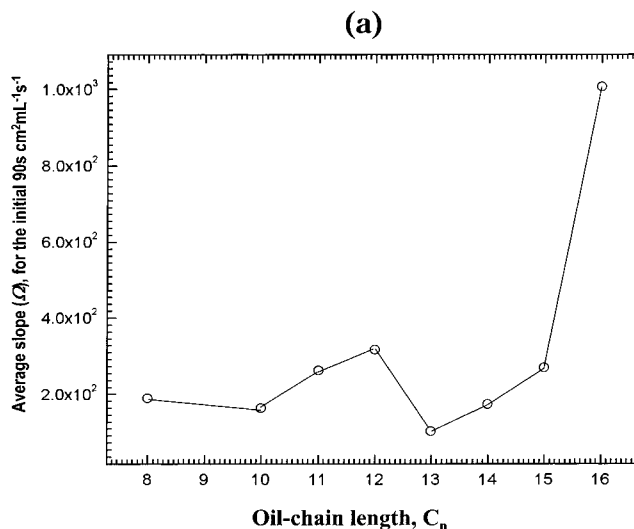


Figure 6. (a) Effect of oil chain length on the spontaneity kinetic parameter (O) of the emulsion process for the system Brij30/oil/water. (b) Effect of oil chain length on the spontaneity equilibrium parameter (F) of the emulsion process for the system Brij30/oil/water. Data were obtained from Figure 4.

Systems containing dodecane, pentadecane, and hexadecane turned out to be the systems with the highest kinetic and equilibrium parameters; therefore, these systems present the highest spontaneity among all the systems studied, that is, they emulsify more easily (see Figure 6a,b).

Finally, it is to be stressed that the “equilibrium” and the kinetic parameters of the spontaneity of the emulsification process for the systems studied yielded the same trends (see Figure 6a,b).

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