

This article was downloaded by: [Celis, Maria-Teresa]

On: 26 September 2009

Access details: Access Details: [subscription number 915329387]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Dispersion Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713597266>

Characterization of Monomer Emulsions in Terms of Droplet Size and Stability: Effect of Emulsifier Concentration

Maria-Teresa Celis ^{ab}; Andrés Gil ^a; Ana Forgiarini ^{ab}; Luis H. Garcia-Rubio ^c

^a Laboratory of Polymers and Colloids (POLYCOL), Chemical Engineering Department, University of The Andes, Mérida, Venezuela ^b Laboratory FIRP, Chemical Engineering Department, University of The Andes, Mérida, Venezuela ^c College of Marine Science, University of South Florida, St. Petersburg, Florida, USA

Online Publication Date: 01 October 2009

To cite this Article Celis, Maria-Teresa, Gil, Andrés, Forgiarini, Ana and Garcia-Rubio, Luis H. (2009) 'Characterization of Monomer Emulsions in Terms of Droplet Size and Stability: Effect of Emulsifier Concentration', *Journal of Dispersion Science and Technology*, 30:9, 1384 — 1389

To link to this Article: DOI: 10.1080/01932690902735595

URL: <http://dx.doi.org/10.1080/01932690902735595>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Characterization of Monomer Emulsions in Terms of Droplet Size and Stability: Effect of Emulsifier Concentration

Maria-Teresa Celis,^{1,2} Andrés Gil,¹ Ana Forgiarini,^{1,2}
and Luis H. Garcia-Rubio³

¹Laboratory of Polymers and Colloids (POLYCOL), Chemical Engineering Department, University of The Andes, Mérida, Venezuela

²Laboratory FIRP, Chemical Engineering Department, University of The Andes, Mérida, Venezuela

³College of Marine Science, University of South Florida, St. Petersburg, Florida, USA

In emulsification processes, the estimation of the droplet size distribution is important data not only because it is linked with the manufacturing process, but also because it is an important parameter affecting the emulsion stability. The aim of this research is to use the ultraviolet-visible transmission spectrum as a tool for emulsion characterization (droplet size and stability) to be a function of monomer concentration, and to verify of emulsion stability using the volume of separated phase's technique. Both techniques are applied to monomer emulsions as a function of emulsifier concentration. Results show correlations between droplet size measurements and stability of emulsions using the spectroscopy technique; results were also found to be in agreement using the cleared volume method.

Keywords Droplet size, emulsion, emulsion polymerization, multiwavelength spectroscopy, stability

INTRODUCTION

As is known, some liquids disperse in another immiscible ones that exhibit more or less stability depending on the application.^[1] The stability against drop coalescence is provided by the presence of a small amount of a third component, the so-called emulsifier, which, in general, is a surface-active agent or surfactant, that adsorbs at the drop interface and produces some interdrop repulsion according to a variety of static and dynamic phenomena.^[2] Macroemulsions are liquid-in-liquid dispersions, with drop size ranging typically from 1 to 100 μm that, in general, are large enough to settle under the influence of gravity.

Received 22 April 2008; accepted 17 May 2008.

The authors thank to the Venezuelan National Research Fund (FONACIT-Grant No. F-2005000175, and to the University of the Andes Research Council (CDCHT-Grant No. I-1040-07-08B) for sponsoring the research program at the POLYCOL (Polymers and Colloids) laboratory.

Address correspondence to Maria-Teresa Celis, Laboratorio de Polímeros y Coloides (POLYCOL), Ingeniería Química, Universidad de Los Andes, Mérida 5101, Venezuela. E-mail: celismt@ula.ve, and Luis Garcia-Rubia, College of Marine Science, University of South Florida, St. Petersburg, FL 33620, USA. E-mail: garcia@marine.usf.edu

In most cases, they are made systems, manufactured with a specification in mind, that is, to generate a population of droplets that dramatically increase the surface area available for mass transport, and as a result, they have not only a profound impact on the rate of reaction and on the final properties of the latex, but also in deciding about the locus of particle nucleation in emulsion polymerization process. The most important parameters affecting the stability of an emulsion is the droplet size and the droplet size distribution of the droplet populations, which are influenced by the emulsification procedure and the type and amount of surfactant. When the drops are formed by effect of mechanical shearing the presence of surfactant reduces the interfacial tension between the two liquids and consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases so that breaking is favored. On the other hand, the adsorption of surfactant onto the freshly produced interface results by forming mechanical, steric, and/or electrical barriers around them. The steric and electrical barriers inhibit the close approach of one droplet to another. The mechanical barrier increases the resistance of the dispersed droplets to mechanical shock and prevents them from coalescing when they collide.^[2] Thus, the surfactant plays a role in the breaking and

coalescence steps, that is, the dynamic balance that determine the drop size.^[3] Much work has been carried out in determining droplet size and stability of emulsions as function of surfactant concentration and the so-called formulation variables^[4-11] but very little experimental work has been reported in the area of characterization of monomer emulsions in terms of droplet size and stability. For instance, monomer droplet size has been determined using osmium tetroxide staining to get cold stage electron microscopy pictures.^[4,12,13] Droplet size of methyl-metacrylate emulsions has been reported utilizing techniques which require a camera and light microscopy.^[14] Conductance measurements have been used to monitor the emulsification process and indicate something about stability,^[15-17] and shelf life stability measurements were used in order to verify conductance as a method to evaluate the stability.^[18] Light scattering techniques are not new and have a long history of development, both in terms of hardware and in terms of the algorithms and methods used for the interpretation of the scattering signal. Commercial light scattering techniques are quite powerful and can be used for online applications. However, standard monochromatic light scattering techniques have difficulties resolving broad droplet size distributions (DSDs) because the scattering contribution from large particles or droplets overwhelms the contribution to the total scattering from small particles when a mixed population of large and small particles is present. Ultraviolet-Visible (UV-Vis) transmission spectroscopy appeared more than five decades ago^[19,20] and has regained interests in the process industry^[21,22] due to recent advances in the algorithms using inverse-solution methods^[23] and the increase and reliability of modern spectrometer, which enables the acquisition of the complete ultraviolet-visible near infrared (UV-Vis-NIR) spectra with excellent wavelength resolution and short measurement times leading to real-time continuous monitoring applications.^[24-26] The resolution in terms of droplet size near infrared is proportional to the size parameter α defined as: $\alpha = D/\lambda$, where D is the particle diameter and λ is the wavelength, leading to spectroscopy measurements over a broad range of wavelengths and a large range for particles analysis.^[26-28] The information is obtained from spectroscopy analysis of a sample measured over a broad range of wavelength and/or with the scattered light measured at one or several observation angles. In the diluted regime, Mie theory can be used for the interpretation of transmission and angular scattering data. This theory describes the absorption and scattering behavior of spherical particles of any size and refractive index and it has shown to be very successful in a large variety of applications.^[5,29,30] Techniques for the estimation of particle size distribution from multi-wavelength spectral data have been reported in the literature.^[19,30,31] However, most of these techniques require that the shape of the particle size distribution

(PSD) be known, or rely on the advantages inherent in the mathematical properties of particle size distributions such as the Lognormal, Gaussian, etc. In addition, most measurement techniques rely on a limited number of wavelengths and do not address issues related to differences in chemical composition.^[20,31] The spectroscopy technique applied herein utilizes a broad wavelength range (190–820 nm), which makes possible particles population analysis with sizes ranging from nanometric to micrometer range^[27,28,32] and this technique is based on the regularized solution to the inverse scattering problem posed by the multiwavelength turbidity equation. As such, it does not require prior assumptions regarding to the shape of the droplet size distribution.^[23,33,34] Systematic spectroscopy study over range of wavelength (190–820 nm) and analysis of emulsions, in terms, of droplet size distribution in the spectral region (300–820 nm) have been successfully obtained and applied to continuous and batch emulsification process,^[26-28,32] and it has been applied to the stability of emulsions.^[10] This quantitative stability criterion is developed from the observation that, if an emulsion is diluted, the dilution ratio or oil concentration necessary to reduce the emulsion droplet size is a measured of its stability. In many instances the concept of emulsion stability is linked with a visual change in appearance or tactility, that is, the time required for a certain amount of emulsion to separate (as a coalesced or clear phase) is a fairly good indication of the stability trend and allows to make some comparisons. If the emulsion is not too stable this may be a nice way to follow up the decay. If it takes too long a time to get visible measurable changes, then some time acceleration tactics would be advised.^[3,7,35] As coalescence proceeds one (or both) of the aqueous and oleic phase tends to clear, then the cleared volume is monitored versus time. When coalescence is completed, the volume value at infinite time of the emulsion (noted V_{∞}) is taken as a reference, and the relative cleared volume (V_c/V_{∞}) is plotted versus time, so that, after complete settling the V_c/V_{∞} ratio varies from zero to unity. The aims of this article is characterize styrene emulsions in terms of droplet size and droplet size distribution, and to study their stability using both a spectroscopy technique as function of the monomer concentration and emulsifier concentration and a method of cleared phase for stability as function of emulsifier concentration.

EXPERIMENTAL

Materials

The ionic emulsifier, sodium dodecyl benzene sulfonate (SDBS) is obtained from Fluka (Buchs, Switzerland). The absence of the characteristic dip prior to the critical micellar concentration (CMC) in the surface tension versus emulsifier concentration curve indicates the purity of this

material. The CMC is $1.4 \text{ g/L} \pm 0.1$. Styrene is obtained from Aldrich Chemical Company (St. Louis, MO, USA) with a 99% of purity. For styrene, the inhibitor is removed by washing several times the monomer with a sodium hydroxide solution (NaOH). The amount of NaOH added corresponding to a NaOH solution: styrene molar ratio of 3:2. After, the inhibited monomer is stored at 4°C . Sterilized de-ionized water is used in emulsion preparation. The equipment utilized for the preparation of the emulsions consists of a 250 ml jacketed reactor, a water bath with temperature controller obtained from Cole Parmer (Vernon Hills, IL, USA), an electric stirrer IKA model RW20DZM.N provided by Works Inc., and a spectrometer (Hp8453) equipped with temperature controller (Peltier).

Methods

Emulsion Preparation

The monomer-in-water emulsions are prepared according to the recipe based on a 34 wt% of monomer, (0.6, 1.2, 3, 4 wt%) of emulsifier. The procedure used for preparation of emulsions is summarized as follows. In a 250 mL jacketed reactor with baffles, the necessary amount of sterilized de-ionized water is added to the bottom of the reactor together with the amount required of emulsifier (SDBS) with mixing until complete dissolution is reached. Monomer is added to the mixture and allowed to equilibrate during 30 minutes, after, this mixture is heated to 25°C with stirring at 500 rpm using a water bath with temperature controller connected to the jacketed reactor and a stirrer equipped with a 4-paddle Rushton turbine impeller during 15 minutes. A sample slip stream of the emulsion is drawn from the reactor and diluted with sterilized de-ionized water at the same process temperature to bring the concentration of the emulsion sample within the linear range of the spectrometer^[10,26–28,32] and the spectra are used for further analysis. At the same time, the other part of the emulsion is used for stability analysis.

Spectroscopy Measurements

Spectra of the emulsions, monitored over the entire wavelength (190–820 nm) are interpreted where no absorption takes place (300–820 nm), leading to the quantitative characterization of the emulsions in terms of droplet size and droplet size distribution.^[27,28,32] The Uv-vis transmission spectra from the liquid-liquid dispersions are recorded using a diode array spectrometer having an acceptance angle smaller than 2° , and a thermoelectric cell holder with a temperature controller with temperature programming capabilities. Prior to recording the spectrum of each sample the spectrometer is zeroed to account for any stray light. To avoid the effect of inhomogeneities in the suspending medium, the background spectrum is taken using the

respective suspending media from the batch utilized in the preparation of the original sample (sterilized de-ionized water). The spectroscopy technique requires as input the optical properties of the components of the emulsion which were reported in previous article.^[28]

Sample Preparation

For dilution experiments of optical technique samples are taken from the top of the reactor by means of a disposable graduated pipette and there is a time lapse of 30 seconds from the time the sample is taken until the first dilution is obtained. The dilution process consists in doing successive dilutions to the sample taken from the emulsion by approximately three orders of magnitude to be within the appropriate absorbance range for measurements (0.01–1 Au). The monomer concentration after of dilution is in the range $1.0 \times 10^{-4} - 10^{-3} \text{ g mL}^{-1}$. The dilutions are done directly in 1 cm path length quartz cuvette and 3.5 ml of volume. Successive dilutions are accomplished using sterilized de-onized water. For stability analysis, 10 ml of emulsion is poured into a graduated test tube. The cleared volume (V_c) is measured as function of time and V_∞ is the same phase volume value at infinite time. Therefore, the relative cleared volume (V_c/V_∞) is plotted versus time.

RESULTS AND DISCUSSION

To quantitative interpretation of spectral data, emulsions of styrene/SDBS/ H_2O are selected. Styrene is of interest for further understanding of the mechanisms of nucleation, and together with the emulsifier (SDBS) ensures the appropriate contrast throughout the spectrum for data interpretation. Figure 1 shows the transmission spectra of styrene/SDBS/ H_2O at 25°C obtained as function of the wavelength and monomer concentration.

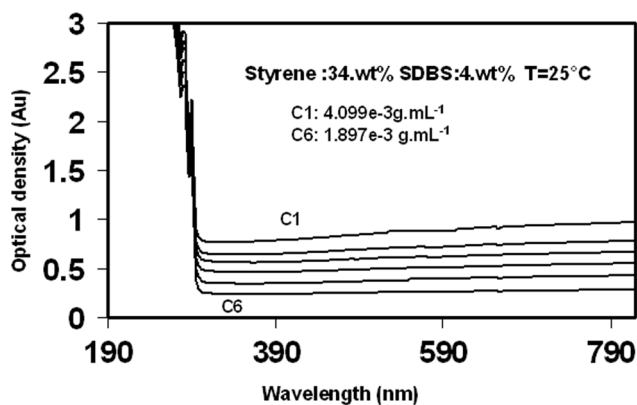


FIG. 1. Optical density of styrene/SDBS/ H_2O emulsions as function of monomer concentration in the range ($4.099 \text{ e-}3 - 1.897 \text{ e-}3 \text{ g mL}^{-1}$), wavelength range of 190 to 800 nm. Styrene: 34 wt%, SDBS: 4 wt%, $T = 25^\circ\text{C}$.

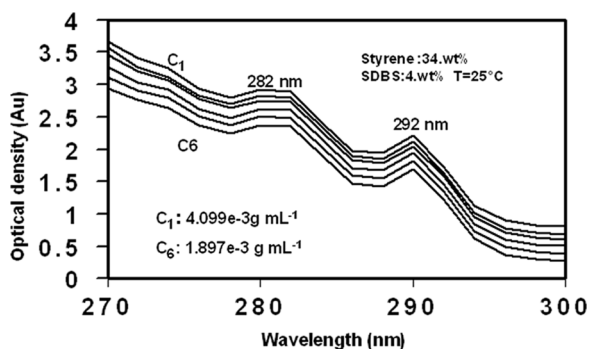


FIG. 2. Variation of the optical density of styrene/SDBS/H₂O emulsions as function of wavelength and monomer concentration (wavelength range: 270–300 nm). Styrene: 34 wt%, SDBS: 4 wt%, T = 25°C.

As can be seen, the optical density decreases with the monomer concentration (dilution process). The region between 300 and 820 nm contains, primarily, information on the scattering behavior of the emulsions, and therefore on the droplet size.^[27,28,32] Figure 2 shows the spectra of the same emulsions in the wavelength range of 270 to 300 nm. As can be appreciated, the region between 270 and 300 nm reflects the absorption due to the phenyl group of styrene which corresponds to the peaks of absorption of styrene (282 nm and 292 nm), which were shown in previous article.^[28] The purpose of Figure 3 is to establish or using spectroscopy as a tool for emulsion characterization: droplet size, droplet size distribution, and stability.^[10,27,28,32] The effect of emulsifier concentration and monomer concentration on droplet size for styrene/SDBS/H₂O emulsions can be appreciated. First of all, it is observed the effect of monomer concentration (dilution process) on droplet size. As can be seen, for emulsifier concentration of 4 wt%, the droplet size is fairly

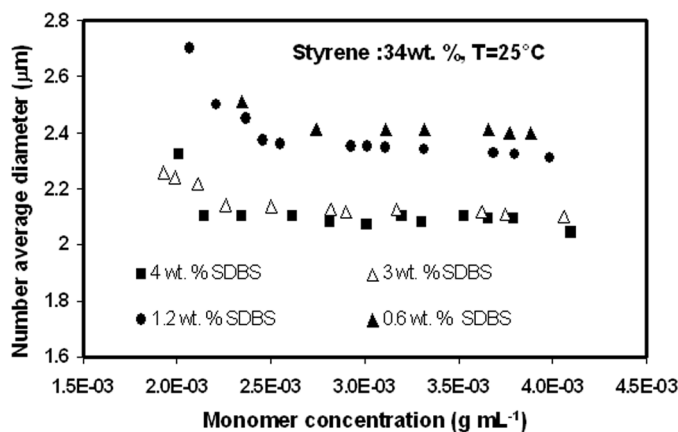


FIG. 3. Variation of droplet size for styrene/SDBS/H₂O emulsions as function of emulsifier concentration and monomer concentration. Styrene: 34 wt%, SDBS: (4 wt%, 3 wt%, 1.2 wt%, 0.6 wt%), T = 25°C.

constant until monomer concentration of $2.15 \times 10^{-3} \text{ g mL}^{-1}$ and after the droplet size increases which is attributed to droplet coalescence. The same is observed for emulsifier concentration of 1.2 wt%, in where the droplet size is approximately constant until monomer concentration of $2.46 \times 10^{-3} \text{ g mL}^{-1}$, then the droplet size increases. Therefore, the dilution range, which the droplet size is maintained, is higher for emulsions with emulsifier concentration (4 wt%). In accordance with the stability criterion,^[10] the more stable emulsion is that of higher emulsifier concentration (4 wt%). Second, it also is shown the effect of emulsifier concentration with the droplet size. As it is indicated, the droplet size of these emulsions undergoes changes with the emulsifier concentration. An increase in emulsifier concentration generally tends to speed up the emulsifier adsorption, which is associated with interfacial tension decreasing and droplet breaking. All of these effects promote the formation of smaller droplets.^[3,27] It can be corroborated in Figures 4 and 5, which show the droplet size distributions as function of monomer concentration and emulsifier concentration of styrene/SDBS/H₂O emulsions at 25°C. As can be appreciated, in Figure 4, there are not significant changes in the breadth of the distribution for dilution range where the droplet size is maintained fairly constant. However, in Figure 5 is observed that the amplitude of the distribution is narrower while the emulsifier concentration is higher for a constant monomer concentration (C_m : $3.6 \times 10^{-3} \text{ g mL}^{-1}$). The smaller the range of sizes, the more stable the emulsion. Since larger particles have less interfacial surface per unit volume than smaller droplets, in macroemulsions they are thermodynamically more stable than the smaller droplets and tend to grow at the expense of the smaller ones.^[2] The model includes the measured and the calculated spectrum that corresponds to the extinction and scattering component respectively. As seen in Figure 6, the excellent agreement between the measured

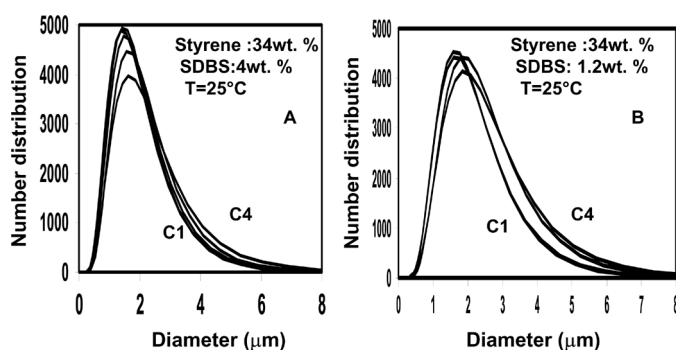


FIG. 4. Variation of number based droplet size distribution for styrene/SDBS/H₂O emulsions as function of emulsifier concentration and monomer concentration (C_1 , C_4). A: ($C_1 = 3.66 \times 10^{-3} \text{ g mL}^{-1}$; $C_4 = 2 \times 10^{-3} \text{ g mL}^{-1}$), Styrene: 34 wt%, SDBS: (4 wt%), T = 25°C. B: ($C_1 = 3.8 \times 10^{-3} \text{ g mL}^{-1}$; $C_4 = 2.3 \times 10^{-3} \text{ g mL}^{-1}$), Styrene: 34 wt%, SDBS: (1.2 wt%), T = 25°C.

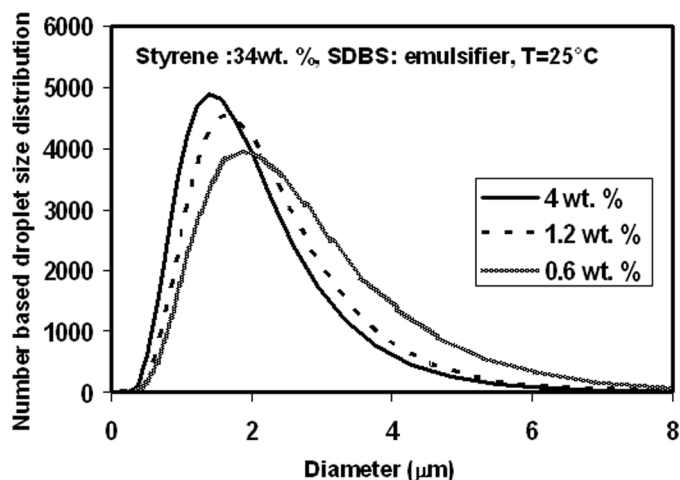


FIG. 5. Variation of the number based droplet size distribution for styrene/SDBS/H₂O emulsions as function of emulsifier concentration. Styrene: 34 wt%, SDBS: (4 wt%, 1.2 wt%, 0.6 wt%), $C_m = 3.6 \times 10^{-3} \text{ g mL}^{-1}$, $T = 25^\circ\text{C}$.

and calculated spectrum of the styrene emulsion at $C_m = 4 \times 10^{-3} \text{ g mL}^{-1}$ in the wavelength range (300–820 nm) show the quality of the model interpretation. To verify the spectroscopy technique as a tool to determine the emulsion properties, the cleared volume method was applied to evaluate the stability of the emulsions.^[35] Figure 7 shows the variation of V_c/V_∞ versus time as function of emulsifier concentration for styrene/SDBS/H₂O emulsions at 25°C . As it is appreciated, all plots have the same tendency; it is a change of cleared volume with the time and emulsifier concentration. Emulsions prepared with lower emulsifier concentration result in higher cleared volumes that these prepared with higher emulsifier concentration. The settling caused by the density differences between the water and monomer phases is proportional to the second power of

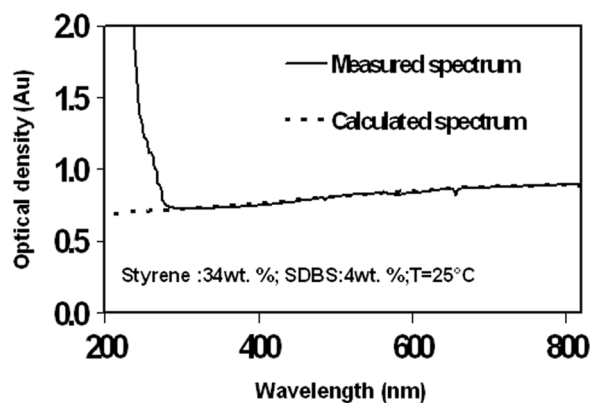


FIG. 6. Measured and calculated spectrum for styrene/SDBS/H₂O emulsion as function of the wavelength at $C_m = 4 \times 10^{-3} \text{ g mL}^{-1}$. Styrene: 34 wt%; SDBS: 4 wt%; $T = 25^\circ\text{C}$.

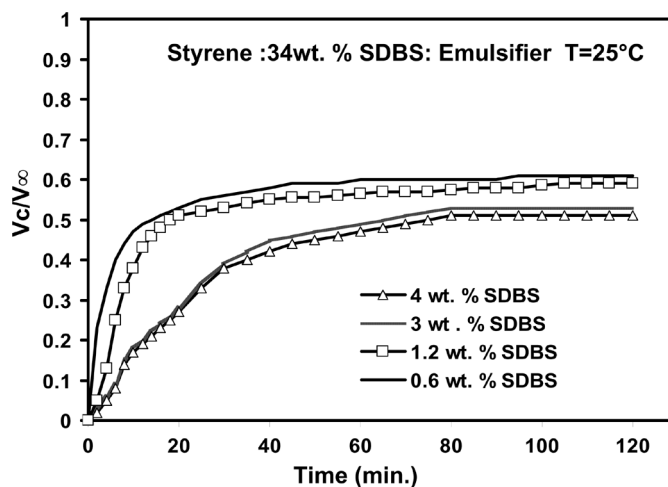


FIG. 7. Variation of the cleared volume for styrene/SDBS/H₂O emulsions as function of time and emulsifier concentration. Styrene: 34 wt%, SDBS: (4 wt%, 3 wt%, 1.2 wt%, 0.6 wt%), $T = 25^\circ\text{C}$.

the droplet diameter (Stokes law).^[36] It is while the emulsifier concentration decrease the droplet size is larger; consequently, the settling velocity is higher leading to higher cleared volume. As it is noted, there is a relation between the droplet size and stability as function of monomer concentration and emulsifier concentration by using spectroscopy techniques and is this relationship is found to be in agreement with the volume cleared technique for evaluation of emulsion stability. Therefore, UV-Vis spectroscopy techniques together with the inversion algorithms have been identified as the experimental tool for the characterization of monomer emulsions in terms of droplet size and stability. Multiwavelength transmission measurements provide the relevant and necessary information of the reaction mixture for identifying the most likely nucleation locus. These studies are ongoing in order to quantify the droplet population in the nanoemulsion range.

CONCLUSIONS

Styrene/SDBS/H₂O emulsions have been characterized in terms of droplet size and stability by using multi-wavelength UV-Vis spectroscopy measurements and found to be in agreement with the assessment of emulsion stability by using cleared volume method. Correlations of monomer droplet size as function of the dilution process and emulsifier concentration show the highest stability for emulsions prepared with emulsifier concentration of 4 wt% resulting in narrower droplet size distribution and lower cleared volume with the time. The characterization of monomer emulsions, in terms of droplet size and droplet size distribution, and stability, as function of emulsifier concentration provides the groundwork necessary for continuing studies on the determination of smaller droplets in

order to identify the most likely nucleation locus which leading to a better understanding of particle nucleation during polymerization reactions.

REFERENCES

- [1] Becher, P. (1977) *Emulsions: Theory and Practice*; New York: Krieger.
- [2] Rosen, M. (1978) *Surfactants and Interfacial Phenomena*; New York: Wiley.
- [3] Salager, J.L. (2000) In *Pharmaceutical Emulsion and Suspensions Drugs and Pharmaceutical Science Series*. edited by F. Nielloud and G. Marti-Mestres, New York: Marcel Dekker, vol. 105, chap. 3, pp. 73–125.
- [4] Azad, A.R., Ugelstad, J., Fitch, R.M., and Hansen, F.K. (1975) *ACS Symp. Ser.*, 24: 1975.
- [5] Sherman, P. (1968) In *Emulsion Science*, edited by P. Sherman; New York: Academic Press; pp. 153–163.
- [6] Hansen, F.K., Baumannofstad, E., and Ugelstad, J. (1976) In *Theory and Practice of Emulsion Technology*, edited by L. Smith; New York: Academic Press.
- [7] Salager, J.L. (1996) In *Surfactants in Solution*, edited by A.K. Chattopadhyay and K.L. Mittal; Surfactants Science Series; New York: Marcel Dekker, vol. 64, p. 261.
- [8] Salager, S., Tyrode, E., Celis, M.-T., and Salager, J.L. (2001) *Ind. Eng. Chem. Res.*, 40 (22): 4808–4814.
- [9] Pérez, M., Zambrano, N., Ramírez, M., Tyrode, E., and Salager, J.L. (2002) *J. Dispersion Sci. Technol.*, 23 (1–3): 55–63.
- [10] Celis, M.-T. and Garcia-Rubio, L.H. (2004) *Ind. Eng. Chem. Res.*, 43: 2067–2072.
- [11] Marfisi, S., Rodriguez, M.P., Alvarez, G., Celis, M.-T., Forgiarini, A., Lachaise, J., and Salager, J.L. (2005) *Langmuir*, 21 (15): 6701–6716.
- [12] Ugelstad, J., Hansen, F.K., and Lange, S. (1974) *Makromol. Chem.*, 175: 507.
- [13] Ugelstad, J., Mørk, P.C., Kaggerud, K.H., Ellingsen, T., and Berge, A. (1980) *Adv. Colloid Interface Sci.*, 13 (12): 101–140.
- [14] Barnette, J. and Schork, F.J. (1987) *Chem. Eng. Prog.*, 83: 25–30.
- [15] Chou, Y.J., El Aasser, M.S., and Vanderhoff, J.W. (1980) *J. Dispersion Sci. Technol.*, 1 (2): 129–150.
- [16] El-Aasser, M.S., Lack, C.D., Choi, I.T., Min, T.I., Vanderhoff, J.W., and Fowkes, F.M. (1984) *Colloids Surf.*, 12: 79–97.
- [17] Brouwer, W.M., El-Aasser, M.S., and Vanderhoff, J.W. (1986) *Colloids Surf.*, 21: 69–86.
- [18] Fontenot, K. and Schork, F.J. (1993) *Ind. Eng. Chem. Res.*, 32: 373–385.
- [19] Kerker, M. *The Scattering of Light and Other Electromagnetic Radiation*; San Francisco, CA: Academic Press.
- [20] Melik, D.H., Fogler, H.S., and H.S. (1983) *J. Coll. Int. Sci.*, 92: 161–180.
- [21] Hassell, D.C. and Bow, E.M. (1998) *Appl. Spectros.*, 52: 18A–29A.
- [22] Gurden, S.P., Westerhuis, J.A., and Smilde, A.K. (2002) *AIChE J.*, 48: 2283–2297.
- [23] Elicabe, G.E. and García-Rubio, L.H. (1989) *J. Coll. Int. Sci.*, 129: 192–200.
- [24] Sacoto, P.J. (1999) Continuous sampling and dilution system for the characterization of concentrated dispersions, M.S. Thesis, University of South Florida, USA.
- [25] Vara, J. (2000) Development of instrumentation for on line monitoring of emulsion polymerization reactions, M.S. Thesis, University of South Florida, USA.
- [26] Celis, M.-T. and García-Rubio, L.H. (2002) *J. Dispersion Sci. Technol.*, 23: 293–299.
- [27] Celis, M.-T. and Garcia-Rubio, L.H. (2008) *J. Dispersion Sci. Technol.*, 29: 20–26.
- [28] Celis, M.-T. and García-Rubio, L.H. (2007) *J. Dispersion Sci. Technol.*, 28: 271–278.
- [29] Allen, T. (1975) In *Particle Size Measurement*, 2nd Ed., edited by J.C. Williams; New York: Chapman and Hall; pp. 314–327.
- [30] van de Hulst, H.C. (1981) In *Light Scattering by Small Particles*; New York: Dover; New York, pp. 63–375.
- [31] Zollars, R.L. (1980) *J. Coll. Int. Sci.*, 74: 163–172.
- [32] Celis, M.-T. (2000) Studies of the initial conditions in emulsion polymerization reactors, Ph.D. Dissertation, University of South Florida, USA.
- [33] Twomey, S. (1977) *Introduction to the Mathematics of Inversion in Remote Sensing and Indirect Measurements*; New York: Elsevier.
- [34] Tarantola, A. (1987) *Inverse Problem Theory: Methods for Data Fitting and Model Parameter Estimation*; New York: Elsevier.
- [35] Salager, J.L., Loaiza-Maldonado, I., Miñana-Pérez, M., and Silva, F. (1982) *J. Dispersion Sci. Technol.*, 3 (3): 279–292.
- [36] Davies, J.T. (1972) *Turbulence Phenomena*; New York: Academic Press.