Korean J. Chem. Eng., **19**(3), 425-430 (2002)

Novel Evaluation Method for the Water-in-Oil (W/O) Emulsion Stability by Turbidity Ratio Measurements

Myung-Geun Song, Sung-Ho Cho, Jong-Yun Kim* and Jong-Duk Kim†

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea
*LG Household & Health Care Research Park, #84 Jang-dong, Yusung-gu, Daejeon 305-343, Korea
(*Received 14 June 2001 • accepted 15 February 2002*)

Abstract—The turbidity ratio method of evaluating the stabilities of water-in-oil emulsions has been established with two wavelengths (450 and 850 nm) by taking the intensity ratio of two beams. The slopes of turbidity ratio of several water-in-oil emulsions with time were calculated to evaluate the emulsion stabilities at different HLB (Hydrophilie-Lipophile Balance), the amounts of emulsifiers, and water contents. The results of the turbidity ratio technique were consistent with the amount of phase separation of emulsions incubated for 30 days at room temperature. From the turbidity ratio measurements, we determined that the required HLB of diesel oil was about 6.0, and that the stability of emulsion increased with the amount of emulsifier. The increasing amount of the water showed a negative effect on emulsion stability. Finally, this method provides a useful tool for the quick evaluation of the required HLB and the condition of emulsification throughout this study.

Key words: Stability of Emulsion, W/O Emulsion, Turbidity Ratio, Required HLB, Droplet Size Distribution

INTRODUCTION

The stabilities of emulsions are very important for various industrial processes and emulsion products, but the evaluation of emulsion stability is not easy. Generally, the kinetics of the emulsion-breaking processes is governed by three different particle loss mechanisms: Brownian flocculation, sedimentation flocculation, and creaming [Reddy and Fogler, 1981]. Particles under Brownian motion collide and then coalesce to form larger particles. At the same time, particles are creaming out due to the difference between the densities of particles and continuous medium. Sedimentation flocculation is due to differential creaming rates of particles and creams out at a faster rate than the smaller ones; therefore, larger particles collide with slowly-moving smaller particles as they cream out.

Such emulsion-breaking processes have been studied extensively by many investigators, and various methods of determining the emulsion stability have been proposed such as droplet size analyses [Treiner et al., 1989; Tadros, 1994], measuring physical properties of emulsion [Tambe and Sharma, 1994; Dreher et al., 1999], and accelerated tests [Forster et al., 1992; Latreille and Paquin, 1990]. Turbidity measurements have also been used to determine the emulsion stability [Kim and Kim, 1988; Song et al., 2000; Lee et al., 1999], and a technique utilizing the spectral absorbance at several wavelengths was proposed to allow the determination within a relatively short period of time [Frenkel et al., 1982; Kaufman and Garti, 1981; Gunji et al., 1992]. The turbidity τ is defined in terms of the attenuation of electromagnetic radiation at a scattering angle of 0°.

$$\tau = \frac{1}{l}\ln(I_0/I) \tag{1}$$

where l is the path length, and I_0 and I are the intensities of the incident and transmitted beams, respectively. Experimental turbidities could be measured with a conventional UV/VIS spectrophotometer, which reads absorbance. If there is no molecular absorption, the turbidity is related to the sample absorbance measured at a wavelength,

$$\tau l = 2.303 \times (\text{absorbance}) \tag{2}$$

For a monodisperse system of nonabsorbing isotropic spheres in the absence of multiple and dependent scattering, the turbidity is given by [Melik and Fogler, 1983; Kerker, 1969]

$$\tau = \pi N r^2 Q(r, \lambda, m) \tag{3}$$

where τ depends on the particle concentration, N, the cross sectional area of particles, πr^2, and the scattering coefficient, Q, which is defined as the ratio of the scattering to geometrical cross sections. The scattering cross section is the total radiation area scattered by a single sphere from an incident beam of unit intensity. This scattering coefficient is, in turn, a function of the particle size, the ratio of the refractive index of the particle μ_p to the refractive index of the medium μ_m, denoted by m, and the wavelength of the incident wave in the dispersing medium, λ. The wavelength λ is equal to λ_0/μ_m, where λ_0 is the wavelength in air. The scattering coefficient is calculated by using the Mie theory of light scattering. Since the turbidity of a polydispersion is the sum of all the contributions over the various particle sizes, the turbidity of the total distribution expressed in integral form is [Kerker, 1969]

$$\tau = \frac{N\lambda^2}{4\pi}\int_0^\infty \alpha^2 f(\alpha) Q(\alpha, m) d\alpha \tag{4}$$

where $\alpha(=2\pi r/\lambda)$ is dimensionless particle size, and $f(\alpha)$ is the distribution function. Therefore, the turbidity of emulsion can be evalu-

†To whom correspondence should be addressed.
E-mail: kjd@kaist.ac.kr

ated with particle size distribution (PSD).

The changes in PSD under conditions of simultaneous flocculation and creaming for various times showed that the PSD shifts to large particle sizes, owing to flocculation of the small particles initially. Since the stability to flocculation increases exponentially with increasing particle size, the smaller particles flocculate quickly to form relatively stable larger particles [Becher, 1988]. Furthermore, the larger particles cream out at a much faster rate than the smaller ones, thereby resulting in an observable shift of the PSD back to the smaller after long time. Finally, the PSD becomes increasingly narrower for longer times because the total particle concentration is now extremely low, thereby resulting only in the slow creaming out of the smaller particles. If the prepared emulsions were stable relatively, these cyclic changes or shifts in PSD would occur slowly. From this point of view, it is possible to evaluate the emulsion stability by measurement of the change of PSD with time and the turbidity method can be a useful one, because the turbidity measurements are rapid and simple.

It is well established that the intensity of light scattering increases with decreasing droplet diameter, and therefore we can estimate the relative size distribution by measuring the ratio of turbidity at two widely separated wavelengths. In fact, the change of turbidity ratio as a function of time exhibits the relative emulsion breaking process by simultaneous flocculation and coalescence more exactly compared with turbidity at single wavelength.

In order to appraise the turbidity ratio technique, several water-in-oil emulsions were tested by using commercially available emulsifiers. The results of this technique were compared with other methods such as droplet size distribution and the amount of phase separation of emulsion.

EXPERIMENTAL

1. Materials and Methods

The oil phase was restricted to diesel (composed of C_{12}-C_{20} hydrocarbon mixture) and was obtained from Hanwha Energy Co. The refractive index of oil measured with Abbé refractometer is 1.469 at 20 °C. No additives were contained in oil and deionized water was used.

For emulsifiers, sorbitan monooleate (Span 80), polyoxyethylene sorbitan monooleate (Tween 80), polyoxyethylene 2-cetyl ether (Brij 52), and polyoxyethylene 2- and 12-nonylphenyl ethers (NP2 and NP12) from Sigma Chemicals were used without further purification. Emulsions were prepared by dissolving the hydrophobic emulsifiers in oil phase and mixed thoroughly with slowly adding the water phase contained with hydrophilic emulsifier. Laboratory homogenizer (Heidolph DIAX 900) was used at 10,000 rpm for 8 minutes. All the emulsions were allowed to age for 24 hours at room temperature and diluted 500 times in oil within 1 minute. Spectral absorbance was measured after dilution by using the Jasco V-570 UV/VIS spectrophotometer. The turbidity ratio was designated as $R(=\tau_L/\tau_S$, L: long wavelength, S: short wavelength).

Droplet size distributions were analyzed by means of dynamic light scattering technique with a Zetaplus instrument (Brookhaven Instruments Co.) after dilution with 500 times. Multimodal size distribution was calculated based on Non-Negatively Constrained Least Square (NNLS) method and the results were plotted as lognormal size distributions. The droplet size variation was monitored with time.

The emulsions were incubated in order to measure the amount of phase separation of the water phase from the oil phase. The freshly prepared emulsions were replaced into 25 ml-cylindrical test tubes and incubated at room temperature. After 30 days, the separation heights were measured and compared with turbidity ratio measurement.

RESULTS AND DISCUSSION

Fig. 1 shows the spectrum of typical optical densities with wave-

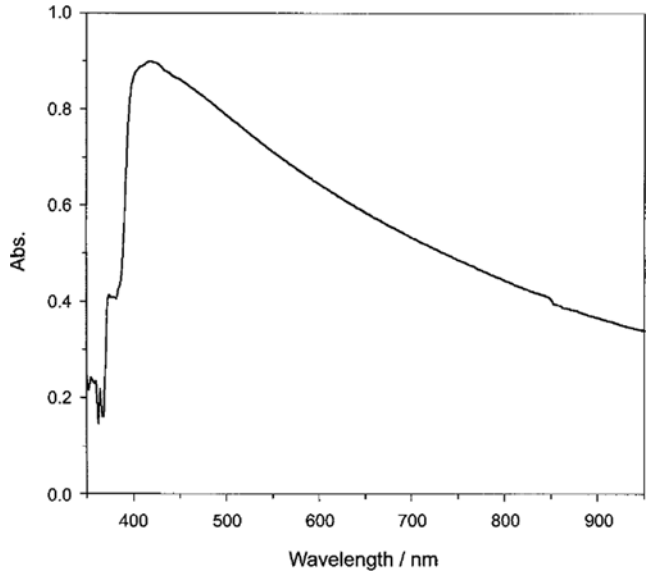

Fig. 1. The spectral absorbance of diluted (×500) emulsion prepared with Span 80 and Tween 80 at HLB=5.5 (2.5 wt% of emulsifier and 10 wt% of water).

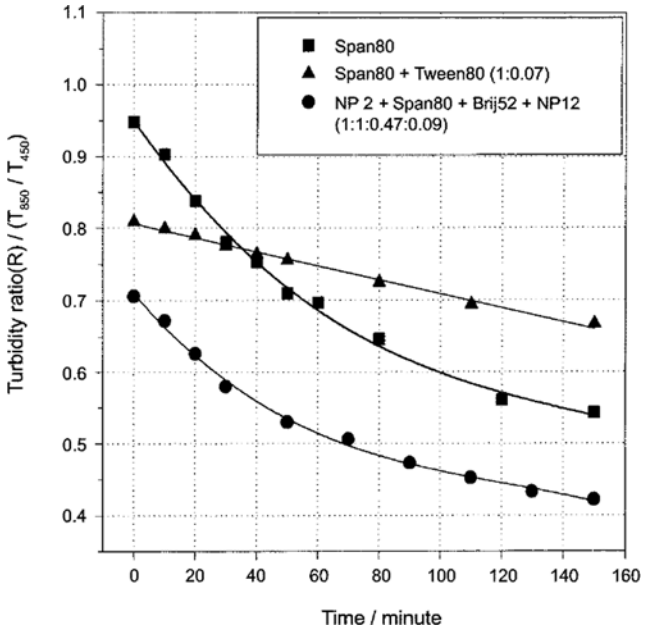

Fig. 2. Change of turbidity ratio, R, in diluted emulsions prepared from different blends of emulsifiers with time (2.5 wt% of emulsifier and 10 wt% of water).

lengths for the diluted emulsions prepared from the blend of Span 80 and Tween 80 at HLB=5.5. The spectral absorbance increases with decreasing of wavelength in the range of 425 nm to 900 nm. The spectral absorbance of diluted emulsions prepared from different emulsifier blends shows similar trends with Fig. 1. Therefore, the R-value was defined as the ratio of spectral absorbance (T) at 850 nm and at 450 nm.

Fig. 2 shows the changes of R-values of diluted emulsions prepared from three different emulsifier blends as a function of time. All emulsions containing 15 wt% of water and 2.5 wt% of emulsifiers. R-values of emulsions of (■) and (●) are more rapidly changed than those of emulsion (▲). Furthermore, there are points of inflection in changes of R with time for the unstable emulsions at around 50 minutes. Therefore, we defined slope of turbidity ratio (=$\Delta R/\Delta t$) as the initial variation up to 50 minutes.

Fig. 3 shows the changes of turbidity ratio for the diluted emul-

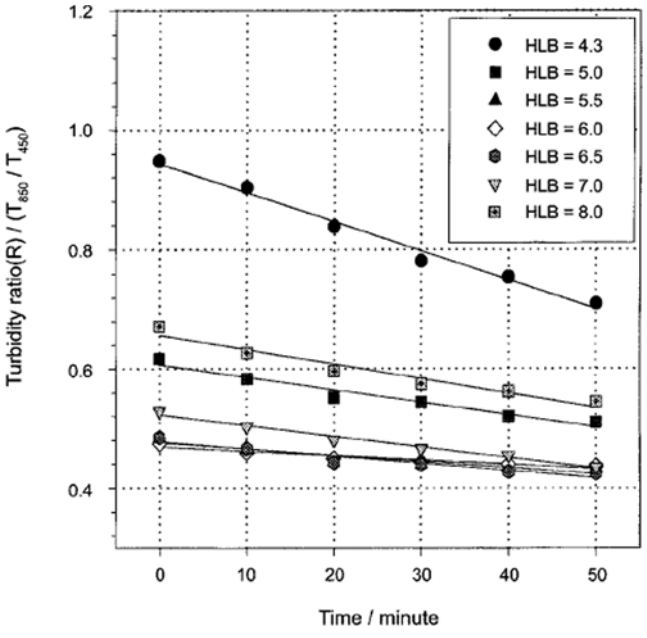

Fig. 3. Change of turbidity ratio, R, in diluted emulsions prepared with Span 80 and Tween 80 (2.5 wt% of emulsifier and 10 wt% of water) with time as a function of HLB value.

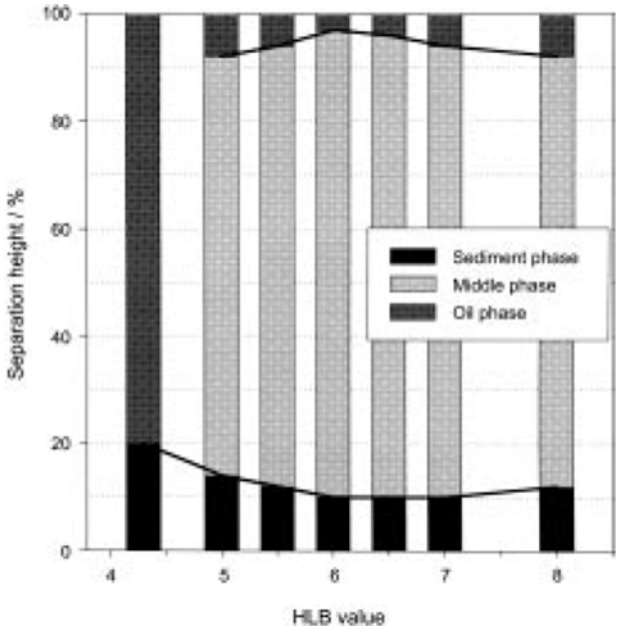

Fig. 5. Inner phase separation of water in diesel oil emulsions prepared with Span 80 and Tween 80 (2.5 wt% of emulsifier and 10 wt% of water) as a function of HLB value after 30 days of incubation at room temperature.

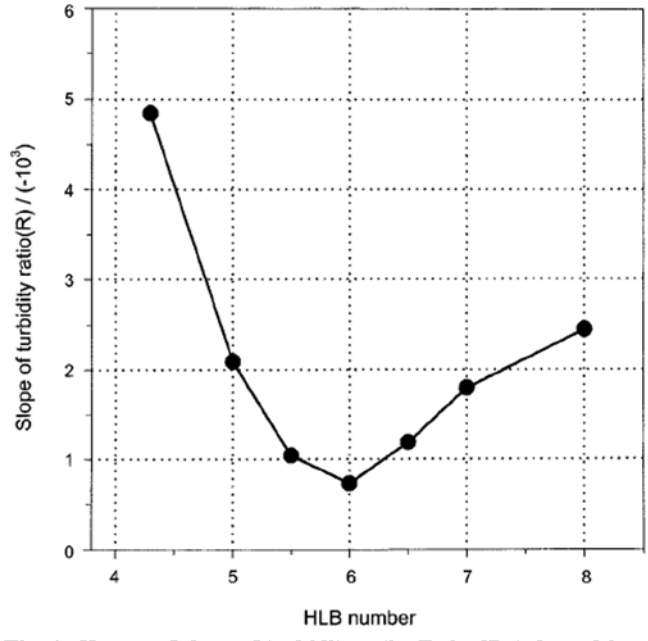

Fig. 4. Change of slope of turbidity ratio, R, in diluted emulsions prepared with Span 80 and Tween 80 (2.5 wt% of emulsifier and 10 wt% of water) as a function of HLB value.

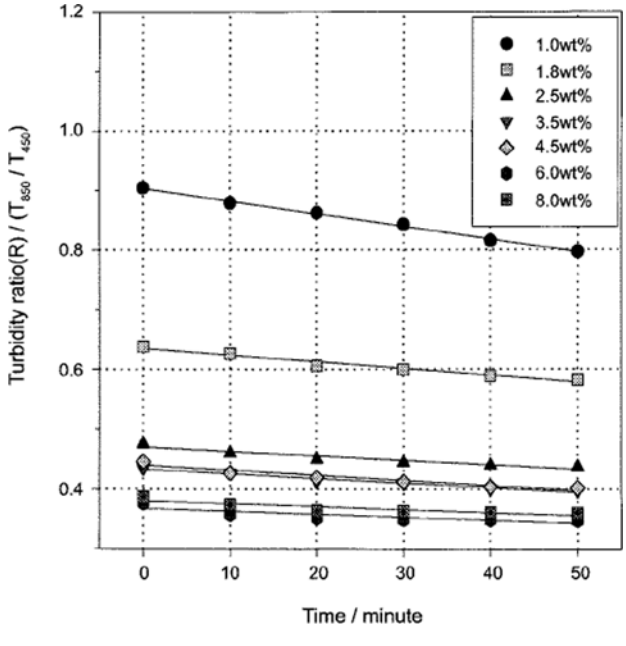

Fig. 6. Change of turbidity ratio, R, in diluted emulsions prepared with Span 80 and Tween 80 (HLB=6.0 and 10 wt% of water) with time as a function of the amount of emulsifier.

sions prepared from Span 80 and Tween 80 blends (2.5 wt% of emulsifier and 10 wt% of water) at different HLB. The turbidity ratios decrease linearly with time. The slopes vary with HLB and are plotted in Fig. 4. It can be seen that the change rate of slope minimized at HLB=6.0, at which the emulsion is the most stable and therefore, the required HLB of oil is 6.0.

After 30 days at room temperature, emulsions were separated into three regions - sediment layer, middle phase, and oil phase - and the minimum separation was occurred at 6.0 of HLB as shown in Fig. 5. These observations were consistent with turbidity ratio measurements and we concluded that emulsion prepared with Span 80 and Tween 80 shows the maximum stability at 6.0 of HLB.

The effect of the amount of emulsifier (Span 80 and Tween 80 blend) in emulsion stability was studied at 6.0 of HLB value and 10 wt% of water content. The variations of turbidity ratio as a function of the amount of emulsifier were measured (Fig. 6), and the slopes were calculated from the linear decreases of turbidity ratios with time. Fig. 7 shows that the slopes of turbidity ratio decreased with the increase of the amount of emulsifier, which is consistent with the stability increase as the emulsifier concentration increase. It is a common phenomenon, found for all emulsions, that stability increases up to a certain emulsifier concentration, and this is well in accord with the result of the above experiment. In fact, the effect of the amount of emulsifier for stabilization of emulsion would be saturated near 6 wt%.

Fig. 8 shows the phase separations of emulsions prepared from different emulsifier content after 30 days at room temperature. The separation amount of emulsion decreases with the amount of emulsifier, and this result is compatible with the change of slope of turbidity ratio.

Finally, Fig. 9 shows the effect of the amount of water. Emulsifiers were fixed at 6.0 of HLB value and 2.5 wt% of emulsifier concentration (Span 80 and Tween 80 used). As the amount of water increased, the stability decreased beyond 30 wt% of water. Apparently, the increase in the water phase has a negative effect on the stability of emulsion. However, the effect of water content on stability of water-in-oil emulsion was relatively small compared with the effect of HLB or the amount of emulsifier, since the slope of turbidity ratio changed only about $0.2\times(-10^{-3})$ as the amount of water increased from 5 to 40 wt%, and equivalent to merely 0.5 wt% change of the amount of emulsifier (from 2.5 wt% of emulsifier).

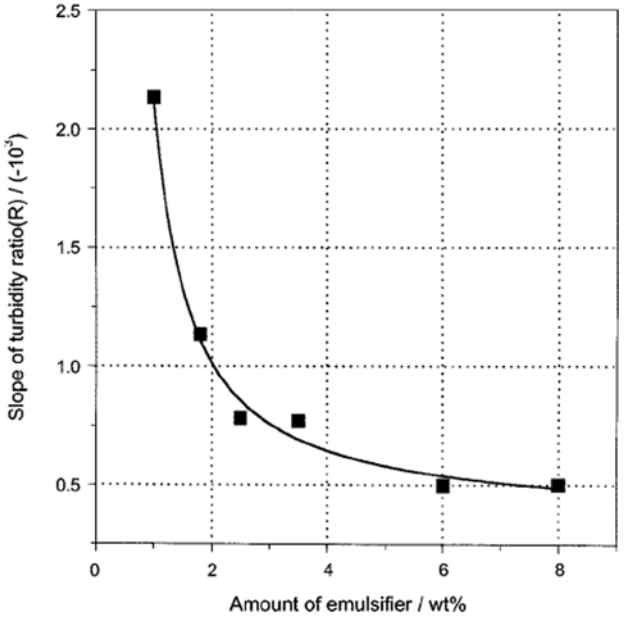

Fig. 7. Change of slope of turbidity ratio, R, in diluted emulsions prepared with Span 80 and Tween 80 (HLB=6.0 and 10 wt% of water) as a function of the amount of emulsifier.

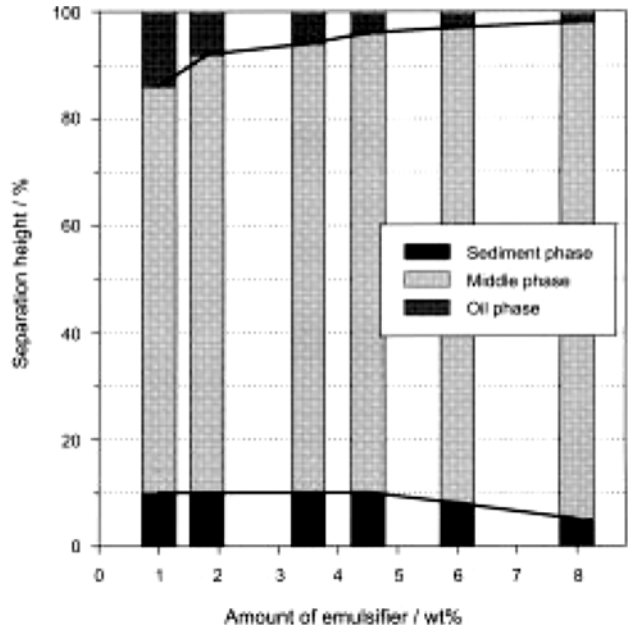

Fig. 8. Inner phase separation of water in diesel oil emulsions prepared with Span 80 and Tween 80 (HLB=6.0 and 10 wt% of water) as a function of the amount of emulsifier after 30 days of incubation at room temperature.

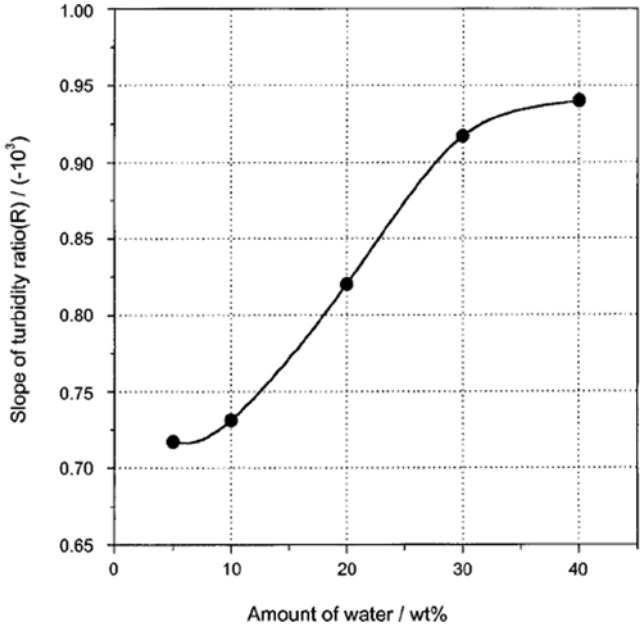

Fig. 9. Change of slope of turbidity ratio, R, in diluted emulsions prepared from Span 80 and Tween 80 (HLB=6.0 and 2.5 wt% of emulsifier) as a function of the amount of water.

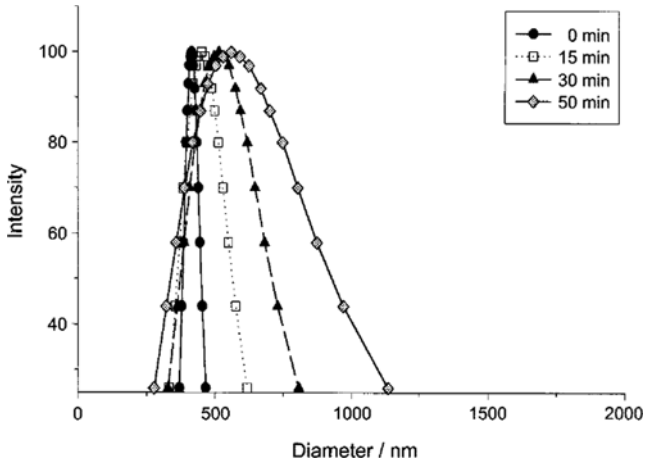

Fig. 10. Time dependence of the droplet size distribution of an emulsion prepared with Span 80 and Tween 80 (HLB=6.0, 2.5 wt% of emulsifier, and 10 wt% of water) after 500 times dilution measured by using a dynamic light scattering technique.

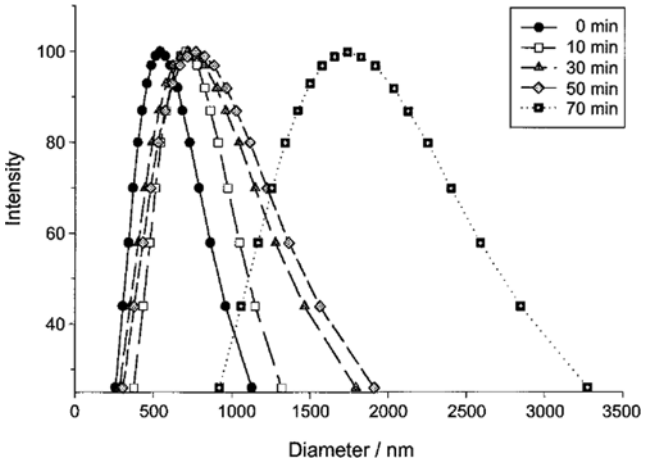

Fig. 11. Time dependence of the droplet size distribution of an emulsion prepared with Span 80 (2.5 wt% of emulsifier, and 10 wt% of water) after 500 times dilution measured by using a dynamic light scattering technique.

Since the turbidity ratio method provides indirect size distribution, we observed the droplet size distribution in diluted emulsion system with time. It is worthwhile to compare two methods. Therefore, the time dependence of the droplet size distribution was monitored by using dynamic light scattering technique.

Figs. 10 and 11 show the time dependencies of the size distribution of emulsion droplets diluted with 500 times in oil phase. Emulsion with Span 80 and Tween 80 at HLB=6.0 was used in Fig. 10, and with Span 80 only (HLB=4.3) in Fig. 11. From Fig. 4, emulsion at 6.0 of HLB is more stable than at 4.3. Both emulsions contain 2.5 wt% of emulsifier and 10 wt% of water. In Fig. 10, the water droplets are small and the size distribution is initially narrow, but the size distribution shifts toward larger particle sizes and becomes broader, owing to simultaneous flocculation or coalescence of the smaller particles with time. In Fig. 11, the droplet size distribution also shifts toward larger size, but much faster and broader than in Fig. 10. Generally, the turbidity decreases with time at any wavelength, because the number of droplets decreases by the emulsion-breaking process. Furthermore, the turbidity at longer wavelength decreases much faster than at shorter wavelength, since the larger particles cream out at a much faster rate than the smaller ones. The more unstable the emulsion is, the faster the turbidity ratio decreases. Therefore, it is a useful, rapid, and relatively simple method for the evaluation of the emulsion stability.

CONCLUSIONS

The validity of the turbidity ratio measurement to evaluate water-in-diesel oil emulsion stability has been examined throughout this study. The turbidity ratios were measured with time after dilution of emulsion, and the slopes of the turbidity ratio were compared. Various factors affecting emulsion stability, such as HLB of emulsifier, the amount of emulsifier and water concentration were tested by using this method. The turbidity technique has been compared with separation amount of emulsion after 30 days incubation at room temperature.

As the results of the turbidity ratio measurements, the required HLB of diesel oil was 6.0 and the stability of emulsion was increased with the amount of emulsifier. The increasing amount of the water showed a negative effect on emulsion stability. These results were well in accord with those of inner phase separation measurements.

Throughout this study, turbidity ratio technique proved to be a simple, rapid, and relatively accurate method for the evaluation of the emulsion stability.

ACKNOWLEDGEMENT

This investigation was carried out in collaboration with Inchon Oil Refinery Co. and was financially supported by this company and BK21 project.

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