Technical

Considerations on Formation and Stability of Oil/Water Dispersed Systems

H.L. ROSANO and **D. JON**, Department of Chemistry, City College of CUNY, New York, NY 10031 and **J.H. WHITTAM**, Shaklee Corporation, Hayward, CA 90045

ABSTRACT

Two systems: (a) a costabilized system of toluene/water/ 1-propanol, and (b) an emulsion system of toluene/sodium dodecyl sulfate/ 1-butanol/NaCl solution are used as examples to provide some general observations on emulsion formation and stability. Phase volume and interfacial tension measurements indicate that the requirement for formation of O/W systems is low γ_i, but for overall stability, γ_i must be positive and of significant value in addition to any steric barrier at the interface. An approximate calculation of the amount of surfactant needed to fill the interface provides a guide for preparation of such systems.

INTRODUCTION

The formulator in the Food, Drug, and Cosmetic Industry often spends long hours developing an easily dispersible yet stable emulsion as the vehicle for his product. The exact and simplest means of formulating such systems is still in question and often becomes the experimenter's trade secret. The following discussion sheds some light on this process and will summarize guidelines for such formulations.

Emulsion formation and stability theories and rules pervade the literature. To this day, there is not one theory or rule which universally preducts every aspect of emulsion formation and stability and also provides easy-to-use formulas for calculation purposes. This only indicates the complexity of such colloidal systems. Earliest theories were based on classical collision theory by Smoluchowski (1,2). Thereafter, theories using the newly developed theory of electrostatic repulsion between the dispersed and continuous phases were applied for emulsion stability. Derjagyin an Landau (3) and Verwey and Overbeek (4) were the first researchers to rigorously explain emulsion stability mathematically according to the double layer (DLVO) theory. The DLVO theory explained many observations particularly aimed at ionic surfactants but, once again, there were great deviations for certain systems. Schulman and coworkers (5,6), in the late 1920s, were reporting stable emulsions which contained mixed complexes of nonionic materials. Their work stressed the importance of the interfacial film being of a condensed liquid nature and thus becoming a barrier to coalescence. Years later, researchers demonstrated that stability of certain emulsions was enhanced when the so-called liquid crystal phase formed at the oil and water (O/W) interface. Friberg and coworkers were able to correlate this to many emulsion systems (7,8).

Of more practical importance was the application of Bancroft's rule in 1913 to nonionic systems (9). He made the observation that the phase in which the emulsifier was most soluble formed the continuous phase of the emulsion. Griffin (10), some years later, further clarified Bancroft's rule relating a balance between the hydrophilic and lipophilic solution tendencies of the surface-active agent. This was later known as the HLB theory, hydrophilic-lipophilic balance, and is well documented by much practical use. Becher (11) expanded much of this work in later years. Along the same line, Shinoda and Saito (12-14) were primarily responsible for the concept of phase inversion temperature or PIT, as it is often called. This is the temperature at which an emulsifier shifts its preferential solubility from water to oil with an increase in temperature. While this work pertains principally to nonionic surfactants, it does provide rules for emulsion formulation.

Another concept based on a more theoretical approach than the HLB theory is that of Winsor's "R" ratio (15). In this theory, a ratio is determined based on the molecular interaction energies on the 2 sides of the O/W interface when interface is saturated with the emulsifier. Beerbower and Hill (16), using Hildebrand's terminology (17), suggested the term "cohesive" for these energies between both the like and unlike molecules and was able to draw practical conclusion on the stability of various emulsifiers in different solvents. This concept is used in the oil and paint industries with a great degree of success.

In this paper, 2 systems are presented to demonstrate other points of consideration on formation and stability of emulsions. The 2 systems are (a) the cosolubilized system of toluene/water/1-propanol, and (b) an emulsion system toluene/sodium dodecyl sulfate/1-butanol/NaCl solution. This latter system was chosen because it can exhibit a range of dispersions and stability levels as a function of concentration of NaCl. This was demonstrated in previous work with phase diagrams.

EXPERIMENTAL

Toluene, propanol, butanol and NaCl were reagent-grade, manufactured by Fisher Scientific Co., Pittsburgh, PA 15219. Sodium dodecyl sulfate was also of reagent grade, produced by J.T. Baker Chemical Co., Phillipsburg, PA 08865. Freshly distilled water was used in all preparations. The interfacial tension measurements were made using a sandblasted Teflon blade and a microforce transducer/amplifier recorder system (Transducer/Amplifier Model 311 A, Sanborn Company, Waltham, MA, recorder Model SREH, Sargent Company, Springfield, NJ) down to a level of 0.25 dyne/cm. Lower measurements in the millidyne region were determined using a spinning top apparatus (University of Austin, Austin, TX). Phase separation was measured in a graduated cylinder after constant shaking by hand and then by settlement for 2 days in a controlled temperature environment of 21.5 C.

RESULTS

Figure 1 is the ternary phase diagram for water/toluene/1-propanol system at 21.5 C. Figure 2 demonstrates the vol-

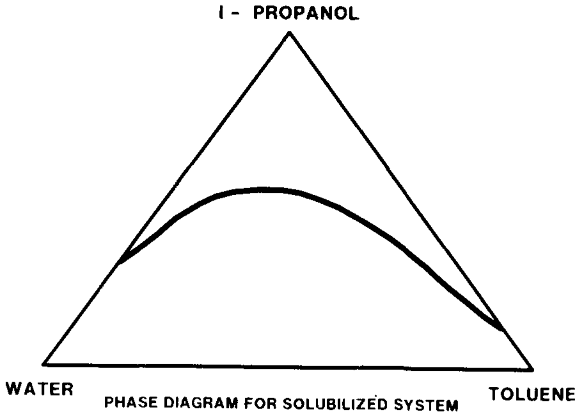

FIG. 1. Ternary phase diagram for water/toluene/1-propanol at 21.5 C.

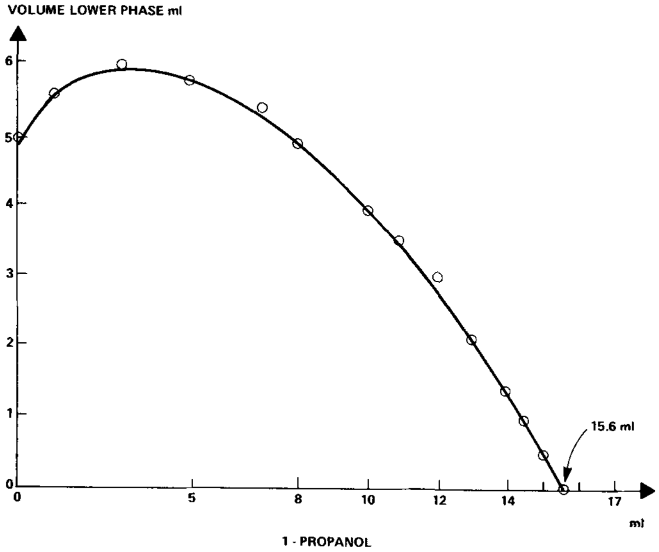

FIG. 2. Aqueous volume as a function of solubilizing agent 1-pentanol. Initial system 5 mL toluene/5 mL water. Temperature 21.5 C.

ume change of the cosolubilized system when 1-propanol is titrated to the suspension system of 5 mL toluene/5 mL water. Following the addition of alcohol, the system was thoroughly shaken and left overnight in an air-conditioned room. The volume (mL) of the lower phase is plotted vs the volume (mL) of 1-propanol added. The water/toluene interface disappeared and became a solubilized system after the addition of 15.6 mL of 1-propanol.

Figure 3 describes the change in interfacial tension as 1-propanol (mL) was added. Curve A shows the region from 0 to 10 mL (left side ordinate in dynes/cm). Curve B shows the region from 8 to 18 mL of added 1-propanol (right side ordinate in millidynes/cm). The apparent change in slope of the curves in these figures is due to a change in scale of the ordinate axis. Extrapolation of curve B to $\gamma_i = 0$ yields a 1-propanol volume of 17.6 mL. This volume of 1-propanol should be noted as being different from the amount necessary to solubilize the system (Fig. 2). Experiments on other water/toluene/alcohol systems is also in agreement with these results. These findings will be presented in a future publication.

Figure 4 relates to the more complicated emulsion system of 1.95% sodium dodecyl sulfate, 3.75% 1-butanol, 46.3% toluene when mixed with varying weight percentages of a stock aq 48% NaCl solution. The percentage NaCl is calculated in the graph as g of NaCl in 100 g of water. Each system was thoroughly shaken in a graduated cylinder and

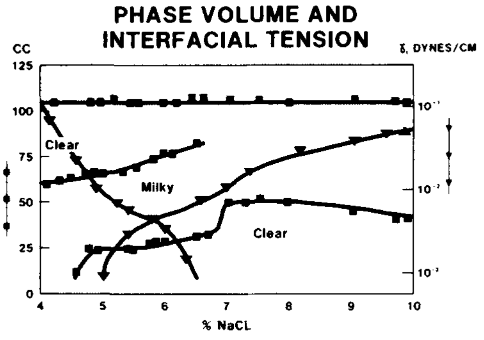

FIG. 4. Change in interfacial tension (▽) and phase volume (□) as a function of weight % of NaCl for the dispersion of toluene/butanol/NaCl dodecyl sulfate/aqueous NaCl. Temperature 21.5 C.

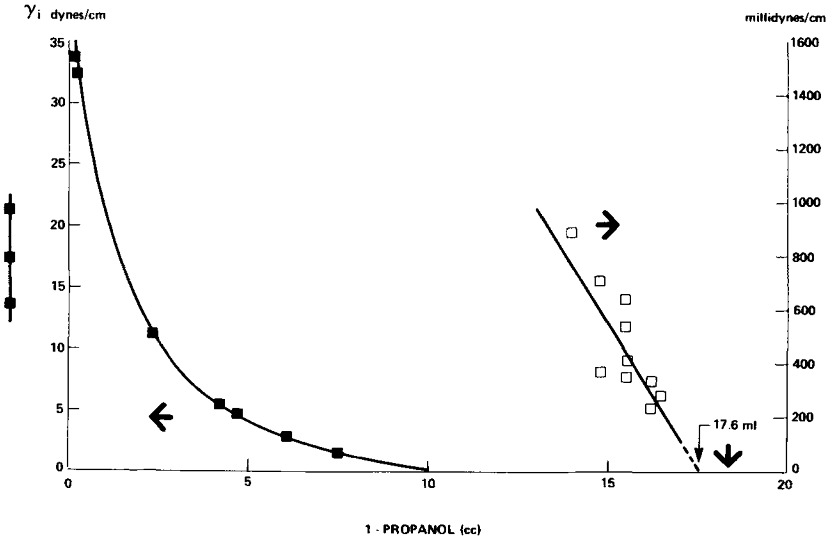

FIG. 3. Change in interfacial tension as a function of volume of 1-pentanol added to a dispersion of 5 mL toluene/5 mL water. Temperature 21.5 C.

allowed to equilibrate for 48 hr at 21.5 C. The total volume for each experiment was measured. Likewise, the total volume in each phase was measured. Between 4.0 and 4.8% sodium chloride, a 2-phase system was formed with the upper layer clear and the lower layer milky, indicating an oil in water dispersion. Above 4.8% NaCl, 3 phases were observed, an upper clear layer, a milky middle phase and a lower clear phase. The volume at each phase was recorded. Above 6.4% sodium chloride, 2-phase regions once again occurred; this time, the upper phase was milky and the lower phase was clear, indicating complete inversion of water and oil. Plotted on the same curve was the measurement of the interfacial tension at the upper phase and the lower phase interfaces. As the concentration of sodium chloride increases, the interfacial tension of the upper phase decreases, whereas that of the lower phase increases.

DISCUSSION

From the results obtained in studying the cosolubilized system, it is obvious that a large amount of cosolubilizing agent (1-propanol) is required to produce a one-phase system. In actuality, in this study, over 10 mL of 1-propanol was added to the 5 mL of water and 5 mL of toluene before the volume of the bottom aqueous phase started to decrease, thus indicating solubilization. It becomes obvious in Figure 3 that the alcohol has, however, a very rapid and significant effect on lowering the interfacial tension well before significant reduction of the lower phase is observed. Thus, it can be concluded that, even though the interfacial tension is small and the work required for the formation of the emulsion is lowered, the stability of the system is still lacking. In addition, the fact that the extrapolated intercept for $\gamma_i = 0$ required 17.6 mL of 1-propanol–yet the system became one-phase after addition of 15.6 mL–further indicates that a + interfacial tension, γ_i, is needed for stability. These facts are in agreement with our previous papers (18-20) in which we have indicated that the work of emulsion and microemulsion formation and overall stability are 2 independent factors. In particular, although formation of the dispersion is enhanced by the low γ_i, the stability is related to the interfacial film formed (whether steric or charged) and, in fact, needs a higher γ_i. In the case of toluene, water and 1-propanol, the film formed is weak and incapable of maintaining a dispersed phase. For this reason, 1-propanol has always been known as a good cosolubilizing agent, but not as an emulsifying agent.

In the study of the emulsion system, below 4.7% sodium chloride, a 2-phase system is formed. The upper clear oil phase and a lower milky phase which displays oil in water characteristics. Above 6.4% sodium chloride, a water in oil emulsion dispersion starts to form, indicated by the milky upper layer and clear lower layer. It should be noted that around 4.7 and 6.4%, slow separation occurred after vigorous shaking of these systems (separation occurred at a much slower rate, requiring well over 24 hr to reach an equilibrium condition). The region from 4.7 to 6.4% sodium chloride produced a 3-phase system with a clear upper layer, a middle milky layer and a clear lower layer. Rapid separation occurred after vigorous shaking of these systems (less than 2 hr) and, in particular, in the middle region of the 3-phase system. Coincidentally, if one plots the overall change in interfacial tension of the upper and lower phases, it is at a minimum in this region. This is interpreted that the lowest possible γ_i produces the finest dispersion, but when γ_i is too low, phase separation occurs rapidly. It is important to remember that spherical shape of a droplet corresponds to minimal interfacial area for a given volume of dispersed phase and minimal interfacial free energy.

A sufficiently low positive value of γ_i is always better for emulsion formation. Nevertheless, below a certain value of γ_i phase separation, sol or gel formation will be produced but not emulsification. Moreover, emulsion stability is, in turn, not dependent on the value of the interfacial tension but solely on the structure of the interfacial film surrounding the individual droplet. Therefore, low interfacial tension is required for formation of the system but a positive interfacial tension appears to be required for stability of any degree. This is similar to observations of Shinoda and Saito (12) who first suggested forming their emulsification process using nonionic surfactants at the PIT temperature (minimal interfacial tension) and then lowering to provide further stability. At the PIT, γ_i is minimally favorable to O/W interfacial area formulation. In our work on microemulsification (18-20), the same concept appears to apply; low interfacial tension is initially required to lower the initial work requirement. However, through transfer and redistribution at the interface, the interfacial tension eventually increases, while the O/W interface curls and droplets are formed, allowing a barrier to form at the interface and preventing coalescence. This observation was also described mathematically by Defay and Sanfeld (21).

METHOD OF PREPARATION OF EMULSION AND MICROEMULSION

Two systems were studied as models in this paper. Other systems have been observed in our laboratory which follow similar patterns (18). From these results, the following recommendations are offered to help the formulator better understand and develop stable opaque or transparent emulsion systems (22). What is described next applies to O/W systems, although a similar reasoning also applies to W/O systems.

(a) A surfactant is selected which is just barely soluble in oil phase; (b) the surfactant thus selected is dissolved into the oil to be emulsified in an amount effective to yield a fine emulsion of the emulsified oil in an aqueous phase; (c) the oil, together with its dissolved surfactant, is added to the water phase and shaken or stirred; (d) finally, a second surfactant is selected to be added while stirring the system in the water phase which is somewhat more soluble in water than the first surfactant to produce a stable emulsion or a microemulsion of oil in water.

The amount of surfactant needed (22) to produce a coarse or transparent emulsion can be estimated by using the equation:

$$n = \frac{3V}{r\sigma} \qquad [I]$$

$$x = \frac{GMW}{6.02 \times 10^{23}\ \dfrac{\text{molecules}}{\text{mole}}} \cdot \frac{3V}{r\sigma}, \qquad [II]$$

where V = volume of dispersed phase (mL); r = radius of dispersed droplet (A); σ = interfacial molecular area of the surfactant (A^2/molecule); GMW = gram molecular weight; x = weight of surfactant in g; n = number of surfactant molecules at the interface.

Selecting primary surfactant and cosurfactant capable of redistribution between the phases is all important. In the process of doing so, an interfacial tension gradient will form, initially lowering the interfacial tension and allowing further dispersion of the emulsion followed by redistribution into the bulk phase, leaving a stabilized film for structural stability of the dispersion.

It is recognized that our recommended procedure may not always produce the desired dispersion because of structural molecular compatibility of the oil phase molecules with the hydrophobic part of the surfactant. In addition, deviations may also be due to hydration of the polar head of the surfactant which is affected by the composition of the aqueous phase. Nevertheless, it serves as a good starting point in forming stable emulsion. More importantly, this work stresses that the formation of dispersed systems is not dependent on simple thermodynamic stability but dependent, at least in part, on the occurrence of kinetic conditions favorable to the dispersion of the dispersed phase into the O/W system.

ACKNOWLEDGMENT

We thank E. Clippinger for helpful technical discussions and the Chevron Oil Field Research Corporation for financial assistance.

REFERENCES

1. Smoluchowski, M., Phys. Z. 17:557 (1916).
2. Smoluchowski, M., Z. Phys. Chem. Leipzig 92:129 (1917).
3. Derjaguin, B. and L.D. Landau, Acta Physicochim. URSS 14: 663 (1941).
4. Verwey, J.W., and J. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier Publishing Co., Amsterdam, 1948.
5. Schulman, J.H., and E.G. Cockbain, Trans. Faraday Soc. 36: 651 (1940).
6. Schulman, J.H., and E. Stenhagen, Proc. Royal Soc. London B 126:356 (1928).
7. Friberg, S., Mandell and J.M. Larrson, J. Colloid Sci. 29: 155 (1969).
8. Friberg, S., and P. Salzom, Kolloid Z. Z. Polym. 236:173 (1970).
9. Bancroft, W.D., J. Phys. Chem. 17:54 (1913).
10. Griffin, W.C., J. Soc. Socmet. Chem. 1:311 (1949).
11. Becher, P., Emulsions: Theory and Practice, Am. Chem. Soc. Monograph, 1966.
12. Shinoda, K., and H. Saito, J. Colloid Interface Sci. 24:10 (1967).
13. Shinoda, K., and H. Saito, Ibid. 32:649 (1970).
14. Shinoda, K., Ibid. 34:278 (1972).
15. Winsor, P.A., Trans. Faraday Soc. 44:376 (1948).
16. Beerbower, A. and M. Hill, McCutcheon's Detergents and Emulsifiers, Allured Publishing Co., Ridgewood, NJ, 1981, pp. 223-232.
17. Hildebrand, J.H., Solubility of Non Electrolytes, 3rd edn., Reinhold Publishing Corp., New York, NY, 1948.
18. Rosano, H.L., T. Lan, A. Weiss, W. Gerbacia and J. Whittam, J. Colloid Interface Sci. 72:233 (1981).
19. Gerbacia, W., H.L. Rosano and J.H. Whittam, in Colloid and Interface Science, Vol II, edited by Kerker, Academic Press, New York, NY, 1976, p. 245.
20. Gerbacia, W., and H.L. Rosano, J. Colloid Interface Sci. 44: 242 (1973).
21. Defay, R., and A. Sanfeld, J. Chim. Phys. Phys. Chim. Biol. p. 895 (1976).
22. Rosano, H.L., J. Soc. Cosmet. Chem. 25:609 (1974); U.S. Patent 4,146,499, (1979).

[Received December 28, 1981]