

Apparent Equilibration Time Required for Surfactant–Oil–Water Systems to Emulsify into the Morphology Imposed by the Formulation. Part 2: Effect of *sec*-Butanol Concentration and Initial Location

Gabriela Alvarez, Raquel Antón, Shirley Marfisi, Laura Márquez, and Jean-Louis Salager*

Laboratory FIRP, Ingeniería Química, Universidad de Los Andes, Mérida 5101, Venezuela

Received January 31, 2004. In Final Form: May 1, 2004

Winsor type I equilibrated surfactant–oil–water (SOW) systems produce o/w emulsions upon stirring. However, if the surfactant is initially dissolved in the oil phase, the attained type after immediate emulsification is usually w/o. If the SOW system is partially equilibrated, it could result in a normal o/w emulsion, as if it were fully equilibrated. The minimum contact time for that to happen, the so-called apparent equilibration time t_{APE} , was previously shown (*Langmuir* 2002, 18, 607) to strongly depend on formulation, surfactant molecular weight, and oil viscosity. The present report shows that it depends on alcohol concentration and location in the unequilibrated system.

Introduction

The relationship between the physicochemical formulation and the emulsion type has been known for a century as Bancroft's rule and experimentally corroborated whatever the formulation variable. If the case of complex morphologies is put aside for the sake of simplicity, it can be said that oil-in-water (o/w; respectively w/o) is associated with Winsor I (respectively II) phase behavior, provided that the surfactant–oil–water (SOW) system is at equilibrium before emulsification takes place and that the water-to-oil ratio (WOR) is not far from unity.^{1,2}

However, if the system is not equilibrated, which is an important case as far as the applications are concerned, things can be quite different. Lin³ reported a long time ago that if the surfactant is initially introduced in the oil phase, the SOW system is likely to produce a w/o emulsion upon immediate stirring, that is, opposite to the expected morphology from the corresponding equilibrated system. This actually resulted in a case of abnormal emulsion, as reported by many other authors,^{4–7} but this time out of equilibrium, as far as the surfactant partitioning is concerned.

In this case, it can be said that with stirred unequilibrated SOW systems the external phase of the emulsion is the one that temporarily contains the surfactant, which is some kind of transient Bancroft's rule.

During the equilibration, the surfactant transfers from the oil to the water phase. The question is how long the unequilibrated SOW system should be left to evolve toward complete equilibration so that enough surfactant was transferred in the water phase to produce a normal o/w

emulsion. The time span after which the emulsion type is the same as if the SOW system were completely equilibrated has been called the apparent equilibration time t_{APE} . This value is quite important in practice because it is some kind of minimum time the phases have to be in contact together to attain the expected emulsion in an industrial process, and it is, thus, directly related with the cost.

In a previous report,⁸ it was shown that t_{APE} strongly depends on formulation and that it decreases as formulation approaches the boundary between Winsor I and Winsor III phase behavior at equilibrium. In some instances t_{APE} was found to be essentially 0, as if equilibration had taken place instantly. The apparent equilibration time t_{APE} was also found to depend on the surfactant molecular weight and on the oil viscosity. The present paper is dedicated to the strong effect the presence and location of alcohol cosurfactant has on t_{APE} .

Experimental Procedures

The surfactant is dissolved in the oil phase, although all studied SOW systems have a physicochemical formulation that corresponds to a Winsor type I phase behavior at equilibrium. Hence, the system is originally unequilibrated, because the surfactant is always introduced in the phase where it will not be when equilibrium is reached. Alcohol is introduced either in oil or in water, as indicated. *sec*-Butanol is selected because it does not shift the physicochemical formulation, but it tends to dilute the adsorbed surfactant layer and to speed up transfer processes.

The physicochemical formulation is changed, either by changing the salinity of the aqueous phase with an anionic surfactant system as in the previous paper or by changing the composition of a mixture of two nonionic surfactants of different HLB values.

The typical emulsion is prepared according to the following procedure, which is slightly more simple than the one previously used.⁸ First, 25 mL of aqueous phase, eventually containing sodium chloride and alcohol, is introduced in a 250-mL high-profile beaker. Then, 25 mL of a solution of surfactant dissolved in oil, eventually containing alcohol, is carefully poured on top of the aqueous phase. The WOR is unity on a volume basis, and the overall surfactant content is 1 wt %. The system is left to rest

* Corresponding author. E-mail: salager@ula.ve.

(1) Bourrel, M.; Gracia, A.; Schechter, R. S.; Wade, W. H. *J. Colloid Interface Sci.* 1979, 72, 161.

(2) Salager, J. L.; Loaiza-Maldonado, I.; Miñana-Pérez, M.; Silva, F. *J. Dispersion Sci. Technol.* 1982, 3, 279.

(3) Lin, T. J. *J. Soc. Cosmet. Chem.* 1970, 21, 365.

(4) Salager, J. L.; Miñana-Pérez, M.; Ramírez-Gouveia, M.; Rojas, C. *J. Dispersion Sci. Technol.* 1983, 4, 313.

(5) Brooks, B. W.; Richmond, H. N. *Chem. Eng. Sci.* 1994, 49, 1065.

(6) Vaessen, G. E. J.; Stein, H. N. *J. Colloid Interface Sci.* 1995, 176, 378.

(7) Zerfa, M.; Sajjadi, S.; Brooks, B. W. *Colloids Surf., A* 2001, 178, 41.

(8) Salager, J. L.; Moreno, N.; Antón, R. E.; Marfisi, S. *Langmuir* 2002, 18, 607.