비이온 계면활성제 수용액에서의 Hydrocarbon Oil의 가용화

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Solubilization of Hydrocarbon Oils in Nonionic Surfactant Solution

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Introduction

The role of mass transport on emulsion stability has been the subject of a number of research efforts that may seem unrelated in many cases. Firstly, some investigations[1] report experiments on the solubilization of oil droplets in micellar aqueous surfactant solutions when the concentration of the transferred oil in the bulk phase is below the saturation limit (hereafter referred to as the equilibrium solubilization capacity). It might be expected that droplet sizes would diminish because oil is transferred from drops to solution, but these studies indicate that the mean size does not change appreciably in time or even increases in some cases.

Secondly, several studies[2] have dealt with the so-called Ostwald ripening, a phenomenon in which bigger drops grow at the expense of smaller drops due to the well-known Kelvin effect[3]. In contrast to the solubilization studies, Ostwald ripening takes place when the bulk phase is slightly supersaturated in the solute that is being transferred.

Finally, when more than one solute is present in the emulsion, differences in concentration among droplets drive mass exchange and induce changes in their sizes[4]. This phenomenon, which has been referred to as compositional ripening[1], is frequently regarded as a particular case of Ostwald ripening[5]. However, this generalization is inadequate because in the case of compositional ripening mass transfer is not dictated by differences in drop sizes. In all these cases, it is necessary to dissolve the transferred materials in the continuous phase, and therefore the kinetics of dissolution play a key role in determining the transient characteristics of ripening emulsions.

Dissolution in water/oil/surfactant systems takes place through mechanisms that occur at the molecular level. Kinetic studies aim at determining the limiting step(s) within such mechanisms that dictate mass transfer rates and transient behavior. Most kinetic studies have been interpreted in terms of (a) the diffusion of the transferred solutes in the bulk as individual molecules[4,6] or incorporated in micellar aggregates[7,8]; (b) the interfacial resistance to mass transfer, which may refer to transport across a surfactant monolayer or some other physical barrier when molecular dissolution prevails[9] or to the adsorption and emission of micelles that act as carriers for the transported compounds[10]; or (c) the molecular diffusion of the solute in the continuous phase and subsequent capturing by surfactant micelles[11]. Even though extensive studies have been performed on solubilization by surfactant solutions, it is not still clear about kinetics of solubilization.

In this work, solubilization experiments were performed for pure hydrocarbons and extended to binary mixtures of hydrocarbons to elucidate the possible rate determining step(s) that dictate mass transfer rates and transient behavior of oil drops in nonionic surfactant solutions of $C_{12}E_8$.

Experimental

The nonionic surfactant $C_{12}E_8$, a pure linear alcohol ethoxylate, was supplied by Nikko Chemical and used without further treatment. Hydrocarbons (n-octane, n-nonane, n-decane, n-undecane and squalane) were obtained from Sigma with a purity of 99%. The solubilization rates of n-octane, n-nonane, n-decane and n-undecane in aqueous solutions of $C_{12}E_8$ were determined at 30.9± 0.1℃ using a technique described previously[12].

The equilibrium solubilization capacities of pure hydrocarbon oils in 2.5 wt% solutions of $C_{12}E_8$ were determined by direct observation of samples under the microscope and the composition of binary hydrocarbon mixtures in micellar aggregates was determined by gas chromatography(GC) method.

Results and Discussion

Since the solubilization concentration of pure alkanes in 2.5 wt% solutions of $C_{12}E_8$ in water is significantly larger than the molecular solubility of pure alkanes in water, it is plausible to assume that most of the oil dissolved is located within micellar aggregates, and that the contribution of molecular solubility to the overall solute concentration in the aqueous phase is negligible. Also, the CMC of $C_{12}E_8$ in water is 7.1×10^{-5}M at 25℃, and therefore, the amount of surfactant forming micelles, can be taken significant error.

Experimental results from solubilization tests with pure alkanes in oil-free 2.5 wt% solutions of $C_{12}E_8$ in water showed that in all cases the drop radii decay linearly in time. On the other hand, squalane drops did not exhibit measurable change in their sizes in similar tests, which indicated negligible solubilization of squalane in the surfactant solution.

The rates of change of drop radii are found to be independent of the initial drop size for pure hydrocarbon oils both at 23℃ and 30.9℃. A linear decay in drop size has indicated that micellar solubilization at the interface limits mass transfer rates. When micellar solubilization at the interface limits mass transfer rates, the specific solubilization rate constant k_o determined for each of the oils indicate that the solubilization rate increases with temperature and decreases with the alkane carbon number(ACN) of the oil. As shown in Fig. 1, the molar solubilization ratio(MSR) for pure alkanes was also found to decrease with the ACN of the oil. It is seen that the ratio of MSR/k_o, which reports the ratio of volume of oil solubilized per mole of surfactant at equilibrium to the volume of oil solubilized per unit time and unit area in the transient solubilization process, remained relatively constant for the different systems and temperatures that were tested, thus suggesting that changes in temperature and ACN affected both MSR and the mass transfer rate analogously. Therefore, the fact that this ratio remains relatively constant strongly suggests that solubilization kinetics is micelle-mediated and that the rates of solubilization depend on the ability of the micelles to adsorb at the interfaces.

Results for the solubilization of octane drops indicated that at low surfactant concentrations (0.25-0.50 wt%) both interfacial resistance to mass transfer and diffusion of micelles carrying solubilized oil significantly influenced the solubilization rate. When the surfactant concentration was increased from 1.0 wt% to 3.75 wt%, spontaneously generated convection in the aqueous phase and Rybczynski-Hadamard circulation within the drops were observed. In such cases convection aided mass transport in the bulk phase and reduced the diffusional resistance, thus making interfacial resistance rate-controlling. The interfacial mass transfer coefficient was proportional to the first power of the surfactant concentration, which suggests that the adsorption/fusion and desorption/emission of micelles carrying oil molecules was the elementary molecular step within the kinetic mechanism that dictated the rates of solubilization.

The ability of the multicomponent model to account for the solubilization of oil drops containing more than one solute with significant solubility in the surfactant solution was tested on mixtures of

n-octane/n-undecane and n-decane/n-undecane in 2.5 wt% of $C_{12}E_8$ nonionic surfactant solutions. For the binary n-decane/n-undecane mixture systems, it is seen that the assumption of ideal solution behavior provided a satisfactory agreement with the data for the transient behavior of drops. On the other hand, moderate deviations from ideal solution behavior were found in the binary n-octane/n-undecane mixture cases, probably due to the partitioning of surfactant between the phases. This agreement was slightly better when the experimental activity was considered instead, as might be expected. In any case, the difference between both trends is within experimental error, thus indicating that the effect of deviations from ideal behavior that are observed mainly for n-octane/n-undecane systems do not affect significantly the transient behavior of drop sizes. This observation is valid for the mixtures of linear alkanes reported in this study, but it may not hold for mixtures of components exhibiting very dissimilar chemical structures.

Equilibrium solubilization tests for the mixtures of n-decane/n-undecane in $C_{12}E_8$ surfactant solutions suggest slightly selective solubilization in favor of n-decane, but the small difference in solubilization rates between n-decane and n-undecane does not allow ruling out non-selective solubilization for this particular system. This is certainly not the case for the n-octane/n-undecane, n-octane/squalane and n-decane/squalane mixtures, for which selective solubilization was conclusively demonstrated. An interesting corollary of the preceding analysis is that the size of drops of mixed oils undergoing selective solubilization can exhibit a transient decay that can be mistakenly interpreted as linear (i.e., non-selective), depending on the resolution of the experimental method or the prevailing experimental conditions. However, GC analysis data in binary systems of pure alkanes strongly suggested selective solubilization for n-octane/n-undecane system and nonselective solubilization for n-decane/n-undecane system (see Fig. 2).

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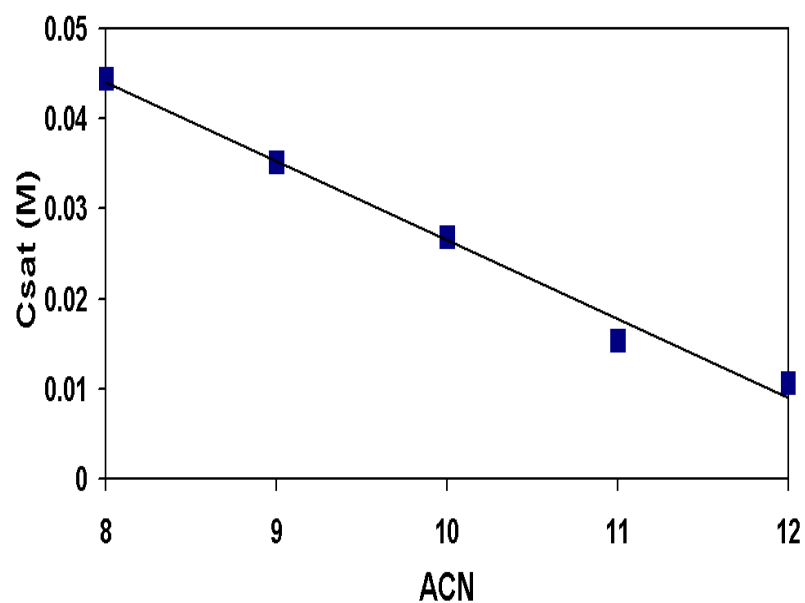
Fig. 1. Equilibrium Solubilization Capacity of n-Hydrocarbons in 2.5 wt% of $C_{12}E_8$ Surfactant Solutions at 30.9℃.
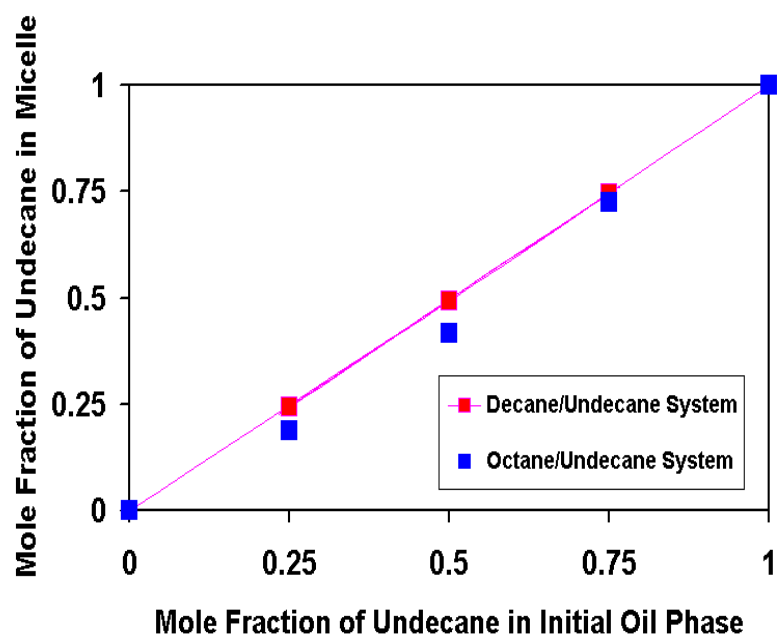

Fig. 2. Equilibrium Solubilization Capacity of Binary Hydrocarbons in 2.5 wt% of $C_{12}E_8$ Surfactant Solutions at 30.9℃.