Solubilization Kinetics of a Triglyceride/n-Alkane Mixture in a Non-ionic Surfactant Solution

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Abstract—The kinetics of solubilization in a non-ionic surfactant solution of pure n-hexadecane, pure triolein and a mixture of the two oils have been investigated. The rates were determined from observations of the dissolution of a single, microscopic droplet, using a drop-on-fibre technique. Conditions were such that negligible saturation of the micellar surfactant with solubilizate occurred. The rate of solubilization of each of the pure oils was found to be independent of time, hexadecane solubilization on a volume basis being about 8 times as rapid as that for triolein. The rate of solubilization of a mixture of the two oils, having a volume fraction 0·69 for triolein, was found to vary in the medium term, the rates apparently being steady both initially and (at a lower value) in the long term. These observations can be related quantitatively to the rates found for the pure oils.

Studies on the solubilization kinetics of mixed oils in surfactant solutions are of interest as they afford quantitative insights into the phenomenon of mixed solubilization, which may include selective solubilization of components from complex mixtures. The captive drop-on-fibre technique has been shown to be a useful tool for studying the solubilization kinetics, in aqueous surfactant solutions, of highly water-insoluble, single component, non-polar oils (Carroll 1981; Carroll et al 1982; Donegan 1984) and the present work is an application of this technique to binary mixtures of such oils.

Previous work on mixtures of oils of *semi-polar* character has suggested that fractionation of one component at the expense of the other may occur (Nagarajan & Ruckenstein 1984; Ward et al 1986). However, a recent study of a mixed, *non-polar* oil system failed to find any evidence for such fractionation (O'Rourke 1983; O'Rourke et al 1987). The present work was intended to investigate further systems of the latter type. It suggests that despite probable mechanistic differences (Carroll 1981), both classes of mixed solubilizate can exhibit fractionation effects and it shows how the present results can be reconciled with those previously published.

Materials and Methods

Materials

n-Hexadecane was BDH Reagent Grade, triolein was Fluka Puriss Grade (~99% purity claimed); both oils were contacted with alumina before use. The non-ionic surfactant n-dodecylhexaoxyethylene ether ($C_{12}E_6$) was a high purity sample from Nikko (Tokyo) and was used as supplied. The cloud point of a 1% w/w solution was 321K. Water was double-distilled from all-glass apparatus. Glassware was chromic acid-cleaned.

Technique

Solubilization rates measured by the captive drop-on-fibre technique are obtained by observing the dimensional

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changes with time of a microscopic oil droplet attached to a fine fibre which is suspended in the surfactant solution. The drop shape is unduloidal (Fig. 1) and analysis (Carroll 1976, 1981) shows that the solubilization rate ρ is given by

$$\rho = -\frac{1}{A}\frac{dV}{dt} = -x_1\frac{dn}{dt},\qquad(1)$$

where A is the interfacial area of a drop of volume V and the other symbols are defined on Fig. 1. Thus the practical determination of solubilization rate reduces to the measurement of two linear dimensions on a series of photomicrographs. (The contact angle for the 3-phase oil-aqueous surfactant-fibre system, if required, is determined by a closely similar procedure (Carroll 1977).) Other experimental details are given by Carroll (1981) and Carroll et al (1982).

Rate data were obtained for three systems: pure n-hexadecane, pure triolein and a 0·69 volume fraction triolein/n-hexadecane mixture. All measurements were at 45°C.

Theory

The rate of solubilization ρ_i^o of a single component i by a micellar solution is defined in terms of volume thus:

$$\rho_i^o = \text{const} \times b_i^o \bar{v}_i,\qquad(2)$$

where b_i^o is the maximum number of molecules of type i which can be solubilized by a micelle and $\bar{v}_i$ is the volume of one molecule of i and the constant is related to the micelle-

$$n = x_2/x_1$$
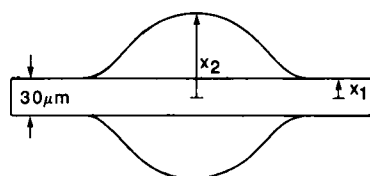$$\Delta n = n(t=0) - n(t) = n_0 - n$$

FIG. 1. Drop-on-fibre shape parameters.

solubilizate interaction rate, i.e. to the micellar flux. The model taken for mixed oil solubilization is one of independent, parallel rate processes involving the separate components of the mixture. The rate of transfer of component i from the bulk mixture to the micellar phase is related to the rate, ρ_i^o, for pure i and to the fractional interfacial area A_i occupied by type i molecules:

$$\rho_i = \rho_i^o A_i \tag{3}$$

In the absence of specific orientation/adsorption effects at the oil/water interface, the area fractions A_i are equal to the bulk volume fractions ϕ_i. Thus:

$$\rho_i = const \times b_i^o \bar{v}_i \phi_i \tag{4}$$

The overall rate is then

$$\rho = \Sigma \rho_i = const \times \Sigma b_i^o \bar{v}_i \phi_i \tag{5}$$

In the above approach it is assumed that individual micelles solubilize molecules of only one type. However, if mixed solubilization occurs in an individual micelle according to the equation

$$b = \Sigma \, b_i = \Sigma \, \phi_i b_i^o \tag{6}$$

application of equation (2) leads to the same rate expression for this situation as well. From a physical point of view, the concept of mixing of components on a micellar scale is (save where saturation occurs at about one molecule per micelle) a reasonable one.

When the solubilizate is a 2-component mixture, as in the case in the present work, equation (6) is conveniently interpreted on a triangular diagram for the system (Fig. 2). If points X and Y represent the compositions of the respective one-component oil/micelle systems, then the compositions expressed by (6) lie on the line XY.

Given the expression (6) for the total number of solubilized molecules in a micelle, it is possible to write for the volume fraction ϕ_i^M of a component in the micelle:

$$\phi_i^M = b_i \bar{v}_i / \Sigma b_i \bar{v}_i = \phi_i b_i^o \bar{v}_i / \Sigma \phi_i b_i^o \bar{v}_i \tag{7}$$

In this equation it is taken that no contribution to ϕ^M is made by the surfactant molecules themselves and the model implied is thus that of solubilization in the 'core', as depicted in Fig. 3. Such a model is likely to be more appropriate for very non-polar molecules solubilized by micelles of surfactants containing long hydrocarbon tails.

Inspection of equation (7) suggests that, in general, $\phi_i^M \neq \phi_i$, so that the composition of the solubilized oil
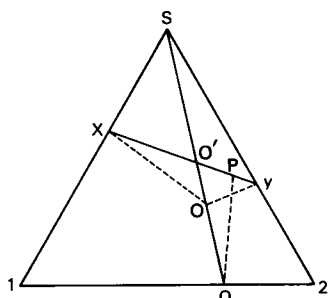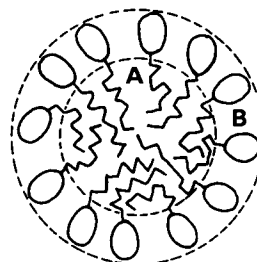

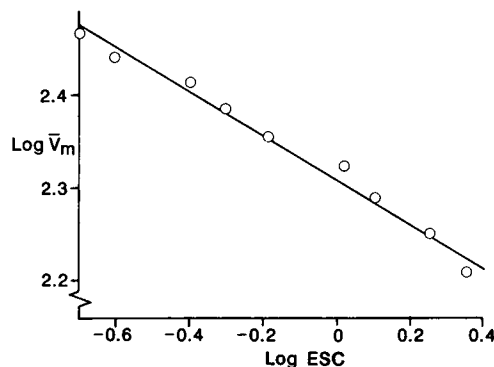FIG. 3. Loci of solubilizates in micelle. Region A = core, Region B = palisade layer.

FIG. 4. Solubilization of n-alkanes in $C_{16}E_6$ (results of Donegan 1984).

mixture differs from that of the bulk. In a 2-component oil system, as solubilization proceeds, the composition of the bulk oil phase changes in favour of one component, while that of the micellar phase alters in favour of the other. The latter component may be said to be selectively solubilized from the bulk oil mixture. An important consequence of this is that the overall rate of solubilization (ρ) changes continually.

If there is a relationship between the number of molecules solubilized, b_i, and the molecular volume $\bar{v}_i$ for each component, equation (7) can be further developed. In general, an inverse relationship between the two is found (cf. McBain & Richards 1946). More particularly, and of relevance to the systems studied in this work, a relation of type

$$b_i = r\bar{v}_i^{-n}, \tag{8}$$

where r and n are constant, appears to hold for core-type solubilization (Fig. 4). The results on Fig. 4 would indicate a value for n of about 4.

If now equations (7) and (8) are combined for a 2-component oil system, the relationship between bulk and micellar phase compositions becomes clearer:

$$\phi_i^M = \phi_1 \bar{v}_1^{-(n-1)} / [\phi_1 \bar{v}_1^{-(n-1)} + \phi_2 \bar{v}_2^{-(n-1)}] \tag{9}$$

$$= 1 / [1 + (\phi_2/\phi_1)S^{(n-1)}] \tag{10}$$

where $S = \bar{v}_1/\bar{v}_2$. A similar expression holds for ϕ_2^M.

It follows at once from equation (10) that when $n > 1$, $\phi_1^M <_> \phi$, according as $S \lessgtr 1$ and that when $S = 1$ (equal molecular volumes), the two compositions are the same. On this model, therefore, a system consisting of two solubilizates of equal molecular volume will not be expected to show selective solubilization.
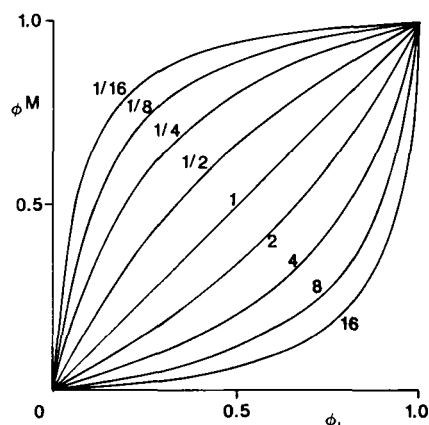

FIG. 2. Diagram for micelle compositions in system surfactant/oil 1/oil 2.

FIG. 5. Dependence of ϕ_1^M on bulk composition (ϕ_1).

The relationship between ϕ_1^M and ϕ_1 is shown in Fig. 5 for $S^{n-1} = 1/16, 1/8, 1/4, 1/2, 1, 2, 4, 8$ and 16. Symmetry about the line for $S^{n-1} = 1$ is apparent. If n is taken to have the value 4, fractionation effects become important for relatively small deviations of the molecular volume ratio S from unity. For example, when $S = 2$, the initial rate of increase of ϕ_1^M, as the bulk phase is progressively enriched in component 1, is some 3 times that for ϕ_1.

The calculated rates

The starting point for the numerical calculation of rates for 2-component oil systems is a combination of equation (2) and (5):

$$\rho = \phi_1 \rho_1^0 + \phi_2 \rho_2^0, \tag{11}$$

in which ρ, ϕ_1 and ϕ_2 are time-dependent. The initial rate of solubilization of each component and the initial overall rate can be calculated from the starting conditions, characterized by ϕ_1 and ϕ_2.

The subsequent progress of solubilization is modelled by considering a succession of short time intervals of duration Δt, during each of which the components are assumed to solubilize at a steady rate. New volume fractions ϕ_1^1 and ϕ_2^1 are recalculated at the end of each interval and these new values are used to determine rates in the next interval.

If at the start of such an interval the respective volumes of the two components were V_1 and V_2 (in an oil drop of volume $V = V_1 + V_2$) and if these changed by ΔV_1 and ΔV_2, respectively, the initial volume fractions

$$\phi_1 = V_1/(V_1 + V_2) \text{ etc.,} \tag{12}$$

become after time Δt:

$$\phi_1 = (V_1 - \Delta V_1)/[V - (\Delta V_1 + \Delta V_2)] \tag{13}$$

If A is the area of the interface across which solubilization proceeds, then

$$\Delta V_1 = A\rho_1^0 \phi_1 \Delta t, \text{ etc} \tag{14}$$

A is either fixed (e.g. if the oil/water interface is the meniscus in a constant-bore capillary) or (as in these systems) is geometrically related to the total volume V of the oil phase. In the present context, the oil is in the form of an unduloidal droplet and tables (Carroll 1976) need to be used to relate A and V.
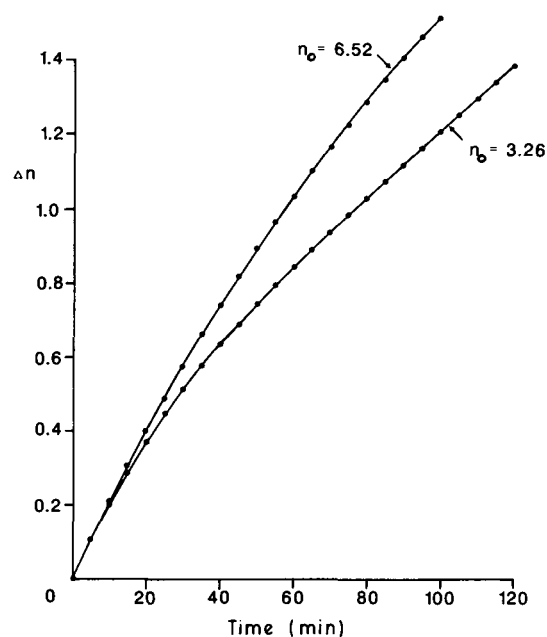

FIG. 6. Expected dependence of Δn on time, for different values of starting drop size n_o.

The results of some computations on these lines are given in Fig. 6 in which the expected behaviour for the particular system studied in this work is presented. The curves are expected to exhibit two important features: (i) they should have initial slopes consistent with the value of the initial rate calculated from equation (11) and (ii) they should have final slopes consistent with the value of the rate obtained for the less solubilized component (triolein, in the present case), because at this stage the residual oil drop is virtually devoid of the other component. The effect of initial drop size (n_o, cf. Fig. 1) on the overall kinetics is shown. Both curves are of similar shape and the initial slopes are equal, but for larger n_o the initial rate of change of the slope is smaller. No effect on the curve shape was observed when the interval Δt was varied between 5 and 10 min: it is only necessary that the Deborah number ($= \Delta t/(\text{characteristic time for overall process})$) for the system is sufficiently low.

Results and Discussion

The experimental data for the pure oils and for the mixture are summarized in Fig. 7 in the form of a plot of Δn (cf. Fig. 1) against time for each system. According to equation (1), the slope of such a plot at any point is proportional to the solubilization rate. The plot is linear for both of the pure oils, but for the mixture it is a curve, concave to the abscissa, which in the limit approaches linearity. This latter behaviour is a consequence of the changing composition of the drop as the relative content of the more rapidly solubilized component decreases, and the final trend towards linearity reflects the nearly total depletion of the drop in this component. The rates of solubilization found for the oils are 0.75 μm min^{-1} for n-hexadecane and 0.13 μm min^{-1} for triolein. The curve for the mixed oils has an initial slope corresponding to a rate of about 0.29 μm min^{-1} and a final slope which gives a rate of about 0.14 μm min^{-1}. The latter is very close to the expected
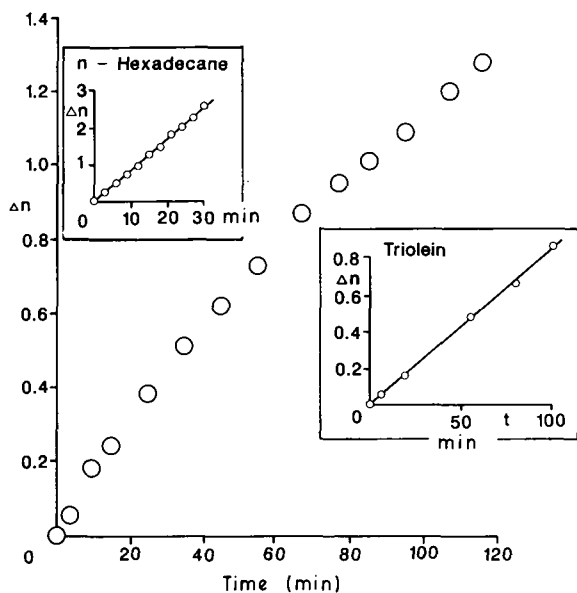
FIG. 7. Experimental dependence of Δn on time: n-hexadecane triolein (insets); (main graph) 0·31 volume fraction n-hexadecane/triolein.
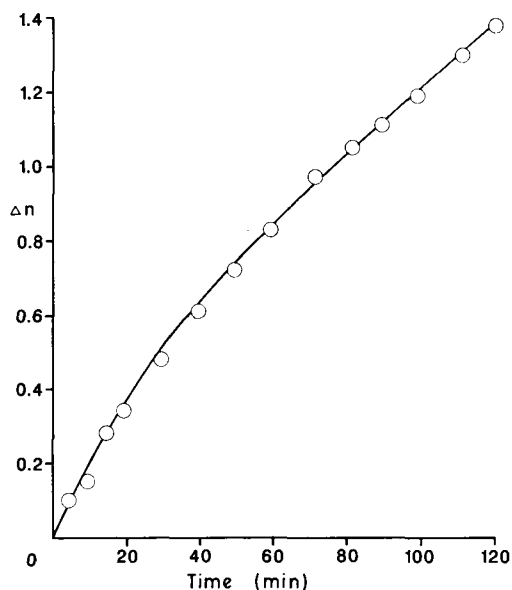

FIG. 8. Comparison of theoretical with experimental results.

value (0·13 μm min^{-1}) while equation (11) predicts an initial rate of 0·32 μm min^{-1}, again in good argeement with that found.

Fig. 8 illustrates the good overall fit to the experimental data of the theoretical curve calculated using $\rho^0_{Hex} = 0·75$ μm min^{-1} and $\rho^0_{Tri} = 0·14$ μm min^{-1}. The close fit of the calculated curve to the experimental data at all stages of the process strongly suggests that the model adopted for calculation

purposes is close to actuality. Thus for the present systems compositions of the mixed micelles should all lie on the line XY in Fig. 2. It can be surmised that in this event, the two oils are solubilized in the same part of the micelle and in view of the non-polar character of the oils, this should be the micelle core region (Fig. 3). In other systems, for example, certain steroid mixtures solubilized in conventional surfactant micelles (Lövgren et al 1978; Lundberg et al 1979), a different pattern of solubilization has been observed, in which one component is apparently solubilized independently of the other. It is then possible to obtain a mixed micelle containing both components in amounts equal to those found for the single component oils. In such circumstances it is reasonable to assume that solubilization of the two components occurs at different sites in the micelle. Such a situation is represented by point O on Fig. 2 and the lines OX and OY represent possible intermediate micelle compositions for this model.

In connection with Fig. 2, it is interesting to note that if the bulk oil composition is represented by a point Q on the 1–2 axis, then points on the line joining this to the S-vertex correspond to micelle compositions for which no selectivity occurs. Thus, if micelles of composition O or O' are in equilibrium with an oil mixture of composition Q, the solubilization process is non-selective. On the other hand, the lines of type QP correspond to selective solubilization. Other relationships can be derived between the points on Fig. 2: these are to be discussed elsewhere.

It remains to reconcile the present results with those found for a mixture of long chain paraffinic hydrocarbons (O'Rourke et al 1987), for which the rate of solubilization was apparently not time-dependent. There are two possible interpretations. O'Rourke et al (1987) attribute the apparently constant observed rate to the possible near-equality of chemical potentials of the two solubilized species. A second interpretation is that the rate data obtained are insufficiently precise to allow the distinguishing between linear $\Delta n - t$ plots and the rather low curvature (previously remarked upon) associated with the early stages for systems with large values of n_0 (cf. Fig. 6). Further work on such systems is desirable.

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