

# Investigations of the solubilization kinetics of binary mixtures of non-polar oils by non-ionic surfactants

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An investigation of the solubilization kinetics of binary mixtures of non-polar oils by a non-ionic surfactant has been made using the drop-on-fibre technique. Variables studied were the oil composition, surfactant concentration and the temperature. Rates vary linearly with the surfactant concentration for all oil compositions. The observed rate during nearly total solubilization of each oil drop was constant, implying that in these systems solubilization is non-selective. The rates increase as the lower consolute (cloud) temperature of the surfactant is approached. Activation energies of the solubilization process are shown to be independent of the oil composition for the system studied. This suggests that the important stage of the process involves dissociation of the surfactant micelles.

The drop-on-fibre technique (Carroll 1981) for studying solubilization kinetics has aided the elucidation of the mechanism for the solubilization of non-polar oils by aqueous surfactant solutions (Carroll 1981; Carroll et al 1982). A common mechanism has been shown to hold for several highly insoluble substrate oils and information about activation energies and certain relaxation processes has been obtained. Solubilization in these systems is considered to occur at the oil/water interface rather than in the bulk aqueous solution and involves micelle dissociation and a subsequent adsorption/desorption sequence, the desorption stage resulting in the depletion of the bulk oil phase.

The solubilization behaviour of oil mixtures is a topic of considerable interest which has to date been investigated in its equilibrium aspects by relatively few authors (Tokiwa 1970; Alhaique et al 1977; Lovgren et al 1978; Lundberg et al 1979; Volkov & Shulitskaya 1981; Thomas & Christian 1981; Nagaraian & Ruckenstein 1981; Christian et al 1982) and not at all in its kinetics. In mixed solubilization systems, the question arises as to how, if at all, the presence of one solubilized component in the micellar aggregate affects the uptake of other components from the bulk oil phase. Thus, in a system consisting of aqueous surfactant micelles in equilibrium with a bulk oil phase of composition  $x_1$  of component 1 and  $x_2$  of component 2, etc., what is the expected composition of the solubilized oil in the

micellar aggregates? Clearly, when one of the  $x_i$  approaches unity, the composition of the micellar aggregate must approach that which is obtained in a micellar system saturated by component 1 only. However, at other compositions of the bulk oil phase, it is possible that the composition of the solubilized oil differs from that of the bulk. It would become possible, if such were the case, to fractionate a mixture of oils by selective solubilization—something which would be of interest in a variety of technological, biological and pharmaceutical areas.

The present paper reports a study of a system comprising a non-ionic surfactant and a mixture of two non-polar hydrocarbons as the substrate oil. A determination of the composition of the solubilized oil in such systems is problematical and has not been attempted here. It has nevertheless proved possible to use the solubilization kinetic data to make inferences about the composition of the micellar aggregates and the results show that in the present system, selective solubilization of one component of the oil mixture does not occur.

## MATERIALS AND METHODS

### Materials

The non-ionic surfactant pentaerythritol dodecyl glycol ether ( $C_{12}E_5$ ) was used as received from Nikko Ltd, Tokyo. High purity of the surfactant was suggested by the absence of a minimum in the surface tension isotherm at the CMC. The non-polar hydrocarbons used were n-hexadecane and 2, 6, 10, 15, 19, 23-hexamethyltetracosane (HMT) (both ex BDH) which were passed through an alumina column before use. Water was deionized and twice distilled.

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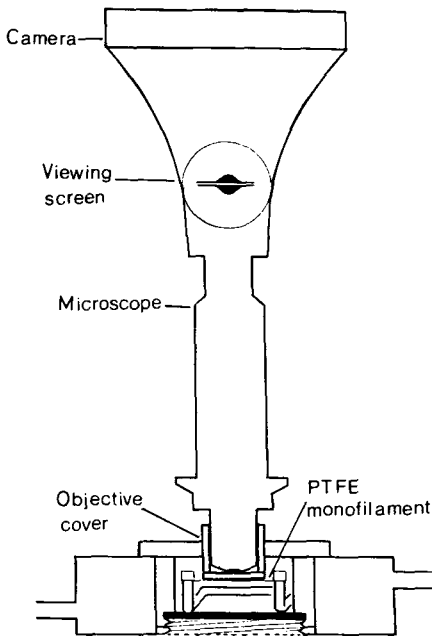


Fig. 1. Experimental scheme.

Glassware was cleaned by the usual chromic acid procedure and non-glass items were cleaned in a Soxhlet-type apparatus containing methanol.

#### Technique

The apparatus (Fig. 1) and the technique were as described previously (Carroll 1981; Carroll et al 1982): a single oil droplet (volume  $\approx 10^{-2} \mu\text{L}$ ) was deposited onto a  $10 \mu\text{m}$  radius PTFE fibre which was suspended in the aqueous surfactant solution and the dissolution of the drop over an appropriate time interval (minutes to days) was followed photomicrographically.

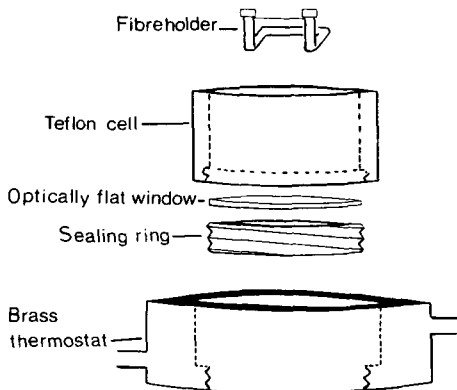


Fig. 2. Cell components.

Direct determination of the drop dimensions by a calibrated eyepiece was possible when the rate was slow. A modified containing cell for the system was used for the present series of experiments. This consisted of a polyfluoroethylene sleeve having an optically flat glass base, the whole being anchored firmly into a brass thermostat jacket (Fig. 2).

Equilibrium solubilization capacities (ESC) for  $C_{12}E_5$  of the two single component oils were determined. 10 mL of a 2% w/w solution of  $C_{12}E_5$  was heated to about 313 K for about 30 min with a small, known amount of the oil and the system cooled at 209 K overnight. Further small amounts of oil were added to the system until the above procedure resulted in the separation of excess oil. The exact ESC was determined by 'back-titration' with neat  $C_{12}E_5$  added in small, known amounts. Equilibrium was confirmed by the stability of the resultant microemulsion over a period of days. No attempt was made to determine the ESC properties of the mixed oil systems.

#### RESULTS

Provided that the contact angle remains sensibly constant, the dimensions of the drop are characterized by the parameter  $n = x_2/x_1$  (Fig. 3). Measured contact angles indeed indicated the required constancy as previously discussed (Carroll 1981). The formal expression for the rate of solubilization is:

$$\text{Rate} = -\frac{1}{A} \frac{dV}{dt}$$

where  $V$  is the drop volume and  $A$  is the oil/volume interfacial area. It was shown (Carroll 1981) that this expression reduced to

$$\text{Rate} = x_1 \frac{dn}{dt} \quad (1)$$

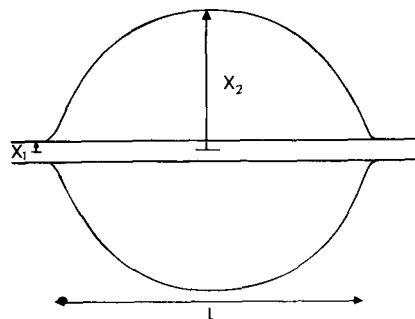


Fig. 3. Drop-on-fibre parameters.

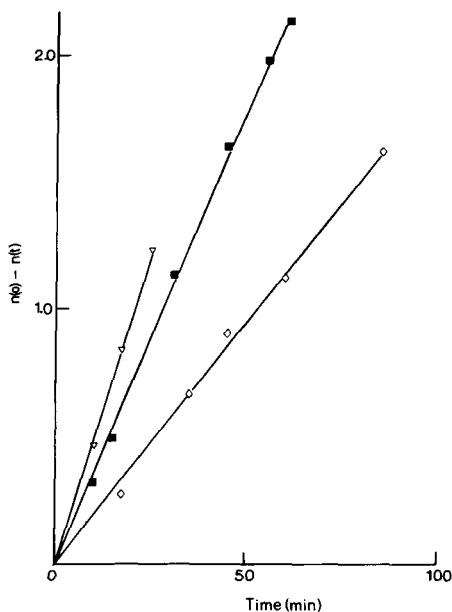


Fig. 4. Time-dependence of parameter  $\Delta n$ . HMT mole fraction: 0.25  $\nabla$ ; 0.50  $\blacksquare$ ; 0.75  $\diamond$ .

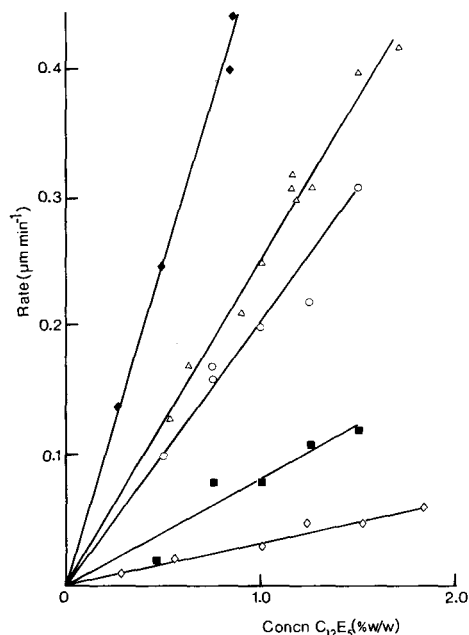


Fig. 5. Concentration-dependence of the rate. HMT mole fraction: 0  $\blacklozenge$ ; 0.25  $\triangle$ ; 0.50  $\circ$ ; 0.75  $\blacksquare$ ; 1.00  $\diamond$ .

for a wide range of values of the parameter  $n$  and the contact angle  $\theta$ . Plots of the quantity  $\Delta n = n(0) - n(t)$  against time,  $t$ , should be linear and have a slope proportional to the solubilization rate. Some typical data are plotted in Fig. 4 for various oil compositions at 1% surfactant concentration and show the expected linear behaviour. A large percentage decrease in the volume of the oil droplet is involved in all cases.

The solubilization rate varies linearly with the surfactant concentration over the range studied (Fig. 5). The slopes of the lines are highest for neat n-hexadecane and lowest for neat HMT, the mixtures showing intermediate values.

Fig. 6 illustrates the temperature dependence of the solubilization rate for different oil compositions. A progressive increase in rate with increasing n-hexadecane content in the oil is evident at all temperatures.

ESC for the solubilization ( $\pm 10\%$ ) of n-hexadecane and HMT at 298 K are 0.80 and 0.186 mole oil/mole  $C_{12}E_5$ , respectively. The solubility of both oils in water is too low for a correction for oil lost to the aqueous phase to be important.

#### DISCUSSION

##### Variation of solubilization rate with time

The data in Fig. 4 show that the rate of solubilization as defined by equation (1) does not vary with time.

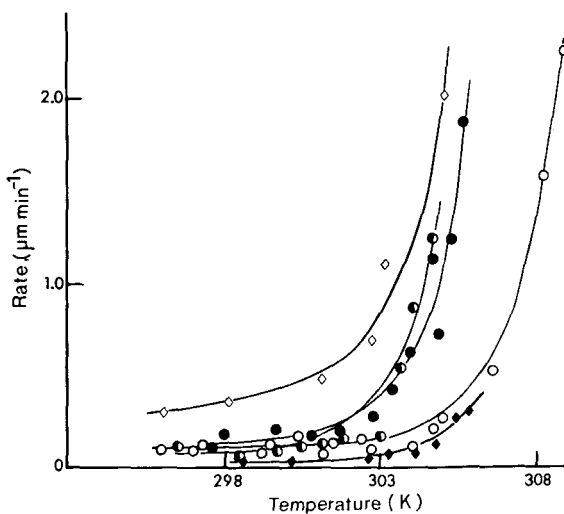


Fig. 6. Temperature-dependence of the rate. HMT mole fraction: 0  $\diamond$ ; 0.25  $\bullet$ ; 0.50  $\bullet$ ; 0.75  $\circ$ ; 1.00  $\blacklozenge$ .

The conclusion from this result is that the composition of the solubilized oil is the same as that of the bulk oil phase, since if, say, n-hexadecane were preferentially solubilized, then the bulk oil phase would become increasingly rich in HMT and the rate of solubilization would fall. A corollary to this is that the technique is a convenient one for detecting

selective solubilization in cases where this may occur, such as systems comprising oils of differing polarity. For the system benzene/cyclohexane/aqueous cationic surfactant, which has been reported (Nagarajan & Ruckenstein 1981) to exhibit selective solubilization in favour of the aromatic molecule, a non-linear time-dependence of rate is observed (Ward et al 1985).

#### *Variation of rate with surfactant concentration*

It was proposed previously (Carroll 1981) that the mechanism for the solubilization process for water-insoluble oils involved the diffusion to, adsorption at, and desorption from the oil/water interface of micelles of the surfactant. A key hypothesis was that only a fraction of the micelles diffusing towards the interface at a given time actually adsorbs (and thence proceeds to desorb with solubilized oil). This is because a prerequisite for adsorption at the oil/water interface is that the surfactant is monomeric, so that the micelle must first dissociate. In fact, most micelles will diffuse away from the interface without dissociation occurring. These considerations can be quantified by multiplying the expression for the micellar phase by a factor which expresses the probability of a micelle dissociating while it is within a distance  $\Delta$  of the interface,  $\Delta$  being a characteristic length for the system.

If the event frequency of a micelle's dissociation is  $\tau^{-1}$ , and the micelle diffusion coefficient is  $D_m$ , this probability factor is  $\tau^{-1} \Delta^2/D_m$  and the effective (adsorbing) micellar flux is  $(C - C_0)\tau^{-1} \Delta$ . The quantity  $\tau$  was erroneously identified (Carroll 1981) with the long micelle relaxation time  $\tau_2$ : in fact,  $\tau$  can have any value up to the value  $\tau_2$ , because  $\tau_2^{-1}$  represents the highest allowable dissociation frequency. There seems to be no obvious lower limit for  $\tau$  which should be constant for a given surfactant at a given temperature; it should not depend upon the nature of the solubilize. The mechanism outlined predicts the linear dependence of solubilization rate on surfactant concentration for a given oil as experimentally observed for both one- and two-component oils (Fig. 5).

#### *The relative rates of solubilization*

A consequence of the invariance of the quantity  $\tau$  with the nature of the solubilize is that the ratio of the rates for two different oils should be wholly independent of  $\tau$  and depend only on the amounts of the oils entering an aggregate at the interface. In a previous study (Carroll et al 1982), the ratio of the solubilization rates of *n*-hexadecane and HMT by

$C_{12}E_6$  (in terms of molecules of oil solubilized) was reported to be about 16:1 at 313 K, whereas the amounts solubilized at equilibrium at the same temperature are only in the ratio of about 7.5:1. For the  $C_{12}E_5$  surfactant systems reported in the present study, the ratio of rates at 298 K is 10:1 and the ratio at equilibrium is 4.3:1. It is apparent that for both  $C_{12}E_5$  and  $C_{12}E_6$  systems, the initial rates of solubilization measured are not in direct proportion to the ESC values. A possible interpretation of this phenomenon was advanced (Carroll et al 1982) where it was postulated that the number of surfactant monomers in the nascent aggregate leaving the interface differed from the number in the final equilibrium state and that the constants of proportionality linking the kinetic and equilibrium values were different for the two oils.

Interpretation of the solubilization rate variation with change in the oil composition at a given surfactant concentration can be made by applying a recent description (Carroll 1986) of solubilization capacities in mixed oil systems (which are subject to the constraint that the oil composition is unchanged). This approach predicts the amounts of the component oils which must solubilize in terms of the amounts that solubilize when each oil is present alone as a single component. Application of this approach to the present systems is complicated by the fact that there is no simple proportionality between the solubilization rate and the equilibrium solubilization capacities (ESC) for *n*-hexadecane and HMT such has been demonstrated (Donegan & Ward 1987) for the homologous series of *n*-alkanes from  $C_8$  to  $C_{16}$ . It is not rigorous, in this case, to use the rate expression

$$\text{Rate} = \text{ESC} \times \text{molar volume} \times \text{constant}$$

where the constant is a kinetic factor, since here this constant is not the same for the two oils and is not predictable. A better approach would be to investigate pairs of *n*-alkanes in the range  $C_{11}$ – $C_{16}$  and results for such systems have in fact now been studied (Faulkner et al, unpublished).

Another approach to the problem is to derive the ESC data needed for theoretical purposes from the ratios of the rates for the pure oils, using these 'kinetic' ESC values to predict ESCs at intermediate oil compositions and thence the rates of solubilization using an expression of the type above. The practical result is that the rate ratio can be predicted as a function of oil composition, the rates for the extreme compositions  $x_1 = 0$  and  $x_1 = 1$  being fitted.

It was shown (Carroll 1986) that in a system

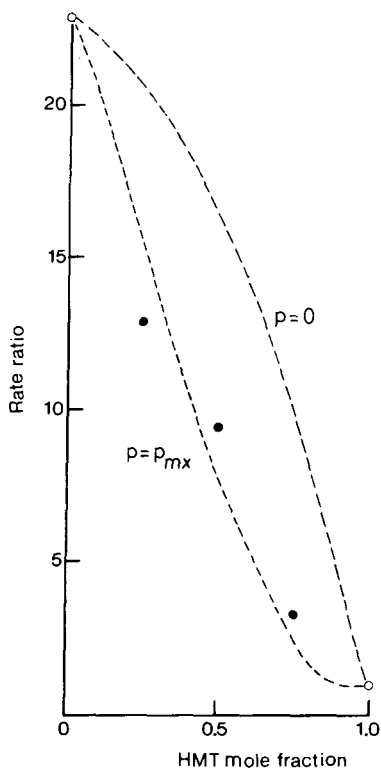


Fig. 7. Composition dependence of solubilization for  $C_{12}E_5/C_{16}H_{34}/HMT$ .

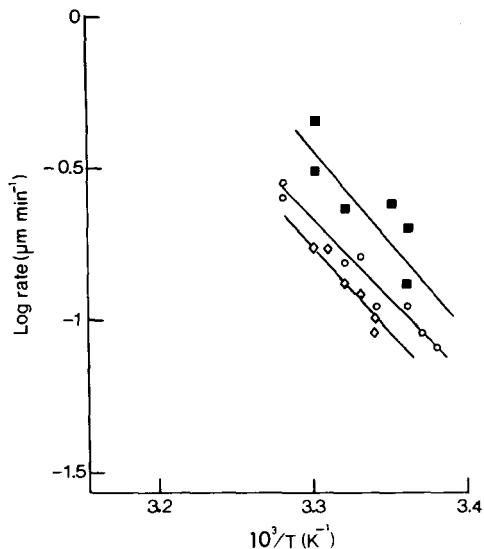


Fig. 8. Arrhenius plots. HMT mole fraction: 0.25 ■; 0.50 ○; 0.75 ◇.

showing non-selective solubilization, a micelle which solubilized  $b_1^0$  and  $b_2^0$  molecules of component 1 and component 2 in single component oil form is from a mixture of 1 and 2 expected to solubilize  $b_1$  molecules of 1 and  $b_2$  of 2, where

$$b_1 = x_1 \{ (x_1 b_1^0 + x_2 b_2^0) - x_1 x_2 P \}$$

$$b_2 = x_2 \{ (x_1 b_1^0 + x_2 b_2^0) - x_1 x_2 P \}$$

and the parameter  $P$ , which may have values in the range 0 to  $(1 + b_2^0/b_1^0)$ , describes the packing of oil molecules in the micelle. High values of  $P$  reflect pairs of molecules which do not pack together easily. Fig. 7 illustrates how the rate ratios predicted using these formulae vary with the value of  $P$  chosen. It is seen that the experimental data are best fitted by a value of  $P$  in the region of the maximum permitted value, which corresponds to severely constrained packing of oil molecules in the micelle. Given the rather poor quality of the data (a consequence of the satellite formation effect), the fit is a reasonable one.

*The effect of temperature*

The temperature dependence of the solubilization rate in the present systems is similar to that observed for other systems (Carroll 1981; Carroll et al 1982) in that the Arrhenius plots  $\{ \log(\text{rate}) - 1/T \}$  are linear (Fig. 8). The slopes of these lines correspond to an activation energy of  $111 \text{ kJ mol}^{-1}$ . This is in good agreement with values previously obtained (Carroll et al 1982) for the system  $C_{12}E_6$  ( $125 \text{ kJ mol}^{-1}$ ). As was previously suggested (Carroll 1981), this activation energy could refer to the process of micelle dissociation, values of this magnitude having been reported by others (Hoffmann et al 1976) for  $C_{12}$  surfactants. A detailed discussion of the temperature-dependence is not possible at this stage, since it would require knowledge of the four-component phase diagram in the temperature range studied. It is clear though that complex changes do occur which affect the surfactant solution consolute temperature in the presence of the oils.

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REFERENCES

Alhaïque, F., Giacchetti, F., Macheth, M., Ricciari, F. H. (1977) *J. Pharm. Pharmacol.* 29: 401-406  
 Carroll, B. J. (1981) *J. Coll. Interface Sci.* 79: 126-135  
 Carroll, B. J. (1986) *J. Chem. Soc. Faraday I*, 82: 3205-3214  
 Carroll, B. J., O'Rourke, B. G., Ward, A. J. I. (1982) *J. Pharm. Pharmacol.* 34: 287-292

- Christian, S. D., Smith, L. S., Bushing, D. S., Tucker, E. E. (1982) *J. Coll. Interface Sci.* 89: 514-522
- Donegan, A. C., Ward, A. J. I. (1987) *J. Pharm. Pharmacol.* 39: 45-47
- Hoffmann, H., Nagel, R., Platz, G., Ulbricht, W. (1976) *Coll. Polym. Sci.* 254: 812-834
- Lovgren, T., Heikius, B., Lundberg, B., Sjoblom, L. (1978) *J. Pharm. Sci.* 67: 1419-1422
- Lundberg, B., Lovgren, T., Heikius, B. (1979) *Ibid.* 68: 542-545
- Nagarajan, R., Ruckenstein, E. (1981) *Sep. Sci. Technol.* 16: 1429-1438
- Tokiwa, F. (1970) *Bull. Chem. Soc. Japan* 43: 939-941
- Thomas, D. C., Christian, S. D. (1981) *J. Coll. Interface Sci.* 82: 430-438
- Volkov, V. A., Shulitskaya, A. I. (1981) *Koll. Zhur.* 43: 752-756
- Ward, A. J. I., Carr, M. C., Crudden, J. (1985) *J. Coll. Interface Sci.* 106: 558-560