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The kinetics of solubilization of single component non-polar oils by a non-ionic surfactant

B. J. CARROLL, B. G. C. O'ROURKE* AND A. J. I. WARD*†

*Unilever Research, Port Sunlight Laboratory, Quarry Road East, Bebington, Merseyside L63 3JW, U.K. and *Dept of Chemistry, University College, Dublin, Dublin 4, Ireland*

The kinetics of solubilization of two non-polar oils (hexadecane and 2,6,10,15,19,23 hexamethyl tetracosane) by a pure non-ionic surfactant (n-dodecyl hexaethylene glycol ether) have been investigated using a recently developed technique. A linear dependence of rate upon surfactant concentration above the cmc and a rapid increase in rate at temperatures close to the cloud point were observed. A previously developed theoretical description of the process has been expanded to account for the observation that the rates for the oils in given systems are not in the exact ratio of the equilibrium capacities of the system for the respective oils. If the effects of changes in aggregation number and shape of the micelle/solubilizate complex are considered, the absolute values of the measured and theoretical rates are in good agreement. Furthermore, the activation energies are nearly equal for the two solubilizates, a result which is in accord with theory. The micelle relaxation time τ_2 is practically independent of surfactant concentration.

The ability of micellar solutions of surfactants to take into solution nominally insoluble material—the solubilization phenomenon—is of practical relevance to fields as diverse as tertiary oil recovery, non-particulate soil detergency, pharmaceutical delivery systems and digestive processes in animals. Many drugs are only sparingly soluble in water, to the extent that they are ineffectual even in saturated solutions. The use of surfactants to disperse a drug on a microscopic scale, as in emulsions, is familiar and effective to the extent that by increasing the interfacial area between the drug and its environment they increase the rate of attainment of equilibrium: the final level of the drug in the aqueous phase is, however, the same. A solubilized drug, on the other hand, is dispersed on a sub-microscopic scale and not only is the interfacial area greatly increased, but the drug is close to being molecularly dispersed and thus available in a more useful form. It is possible that the rate of digestion of fatty foods is regulated by similar considerations and the application of solubilization in these two areas is illustrated in the use of non-ionic actives for the extraction of oil-soluble vitamins in vivo and in the role played by the bile acids in the digestive process.

Studies of the solubilization process have, until recently, been limited to the determination of the equilibrium or saturation solubilization levels in a system and to the effects of sundry variables on this quantity. In this kind of work the rate of equilibration is very slow, and in spite of the mechanistic and other information potentially available, the kinetics of the process have been little studied. Historically speaking, this is because such studies must be made on finely dispersed systems (the rate is too low to be measurable otherwise) and require the accurate measurement of the total volume and interfacial area of the dispersal phase as a function of time, an experiment which is very tedious indeed without the most modern hardware. The difficulty can now be overcome if the latter is available, or else an alternative technique (cheaper by several orders of magnitude) recently described (Carroll 1981) can be used.

† Correspondence.

MATERIALS AND METHODS

Materials

The non-ionic n-dodecyl hexaethylene glycol ether ($C_{12}E_6$) was used as obtained from Nikkol Co, Tokyo, Japan. G.l.c. showed it to contain about 2% of the E_5 homologue, but indicated that it was homologous in alkyl chain length. This last result was supported by the absence of a minimum in the surface tension at about the c.m.c. ($9{\cdot}8 \times 10^{-5}$ mol dm^{-3} at 298 K (O'Rourke 1980)). The cloud point of 1% active in water was 322 K.

n-Hexadecane and 2,6,10,15,19,23 hexamethyl tetracosane (HMT) were BDH reagent grade and were passed through alumina-packed columns before use.

Water was twice distilled, the second time from alkaline permanganate and had a surface tension of 72·78 mNm^{-1} at 298 K.

All glassware was subjected to chromic acid cleaning followed by copious rinsing with water and non-glass parts coming into contact with solutions were cleaned in solvents. A Soxhlet apparatus (without the paper thimble) containing ethanol was used from a late stage in this work as a preferred cleaning method for non-glass parts.

Solubilization rate

The technique is outlined below, but is fully detailed by Carroll (1981). Referring to Fig. 1, a fine PTFE monofilament, 10 μm radius, mounted in a glass frame, is immersed in about 40 ml of water contained in a shallow, glass cell which is mounted on the stage of a conventional microscope. The cell is thermostatted via a water jacket blown integral with the cell and fed by an external water bath. The lower part of the microscope, including the stage, is enclosed in a Perspex glove box fitted with an air thermostat. Using a micro-syringe fitted with a very fine glass jet and held in a micromanipulator (also in the glove box), a single droplet of the solubilizate (≈0·01 μl) is placed on the fibre. The fibre is now brought into focus in the microscope, the objective of which is fitted with a glass sheath based with an optical flat and which can be adjusted to bring the base very close to the droplet. The appropriate amount of surfactant, as a concentrated solution, is then mixed in, using an all-glass syringe (10 ml) for both the addition and the mixing. The droplet is seen to slowly decrease in size (without any sign of interfacial turbulence, etc). The process is followed for times in the range about 1 min to several hours.

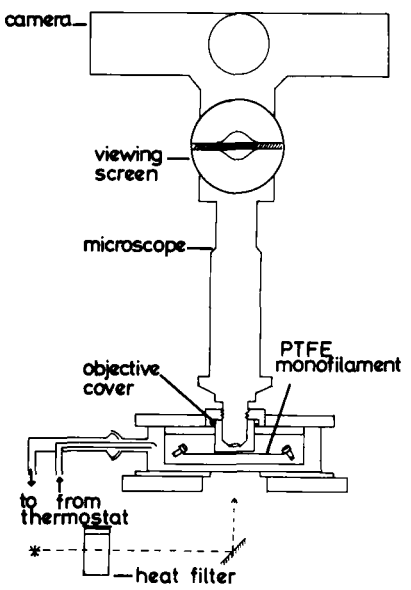

FIG. 1. Apparatus for solubilization rate measurement.

The profile of the drop-on-fibre system is unduloidal in respect of the liquid interface and can be described quantitatively in terms of the three linear parameters indicated in Fig. 2 (Carroll 1976). It has been shown elsewhere (Carroll 1981) that in most systems the rate of solubilization A^{-1} dV/dt (A = interfacial area, V = volume) is given to a very good approximation by the expression $x_1 dn/dt$ ($n = x_2/x_1$, cf Fig. 2). Thus two linear measurements, x_1 and x_2, made on a series of photographs suffice to determine the solubilization rate.

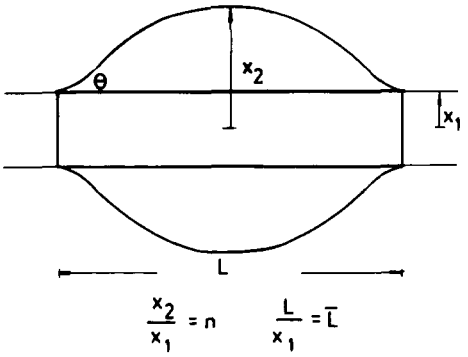

FIG. 2. Profile of drop-on-fibre system with characteristic parameters.

Equilibrium studies

Phase diagrams published for the system n-decane/H_2O/$C_{12}E_6$ (Friberg et al 1977) indicate that up to fairly high active contents the amount of oil solubilized is proportional to the active concentration. The present systems showed this behaviour and it was found convenient to work with 3% w/w $C_{12}E_6$ solutions. An attempt was made to determine the phase diagram for this active concentration as a function of oil content and temperature, concentrating on the cloud point transition and on the saturation point for solubilization, but it was found that equilibration times for the latter phase change were so long (in the case of HMT, sometimes days) that only the solubilization capacity determined at 313 K (for comparison with the rate studies made at that temperature, cf Fig. 3) was considered to be reliable.

Equilibrium was deemed to have been established when the presence of oil droplets could no longer be detected under the microscope. This point was found not to correspond to the apparent establishment of an isotropic phase as judged by eye, especially in the case of HMT, and could lead to serious errors in a phase diagram determined in the latter way.

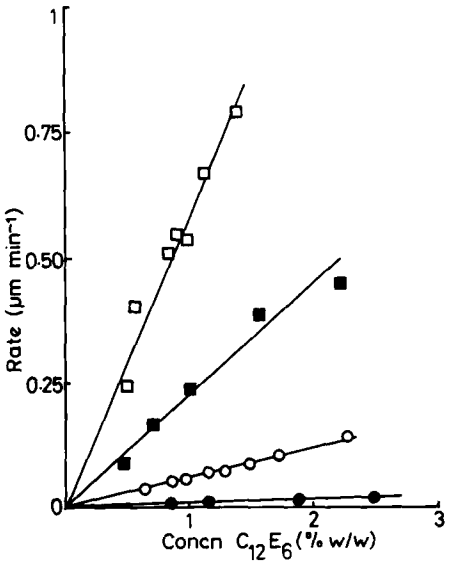

FIG. 3. Rate as a function of active concentration for different oils and temperatures.

RESULTS

Rates of solubilization were found to be linear in surfactant concentration above the cmc (Fig. 3) with no measurable rate below the cmc. This is the same behaviour as found previously (Carroll 1981). The lower molecular weight oil gives the line of highest slope at each temperature.

The slopes of the four lines are: HMT, 298 K: 0·010: 313 K: 0·062; n-hexadecane, 298 K: 0·225; 313 K: 0·576 μm min^{-1} per 1% $C_{12}E_6$. The ratio of slopes for the two oils on a molar basis is about 39:1 at 298 K and 16:1 at 313 K.

Fig. 4 shows that the rate is in all cases an increasing function of temperature and that it increases rapidly as the cloud temperature is approached. The rate for hexadecane is greater than that for HMT at all temperatures within the range studied.

The equilibrium solubilization studies were made only for 313 K and must be regarded as subject to an unknown but fairly large experimental error. The

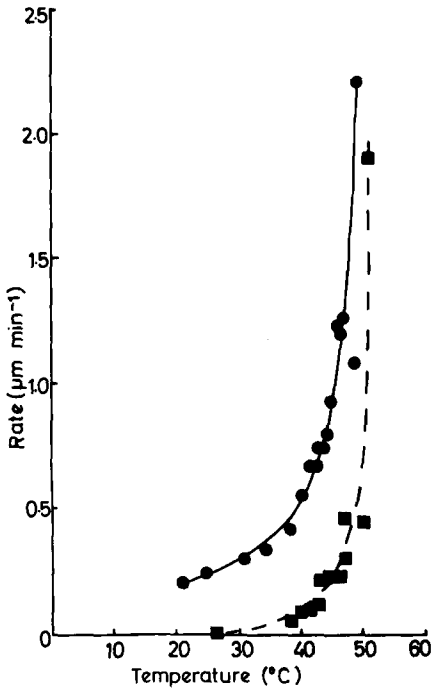

FIG. 4. Rate as a function of temperature: n-hexadecane (●) and HMT (■) (1% w/w $C_{12}E_6$).

3% active solution was in equilibrium with approximately 0·39% w/w HMT or with 1·5% n-hexadecane, giving equilibrium solubilization capacities of respectively 0·136 mole HMT or 1·011 mole hexadecane per mole $C_{12}E_6$ at this temperature, a ratio of about 7·5:1 for the two oils on a molar basis.

DISCUSSION

A mechanism for the solubilization of sparingly-soluble solubilizates has been proposed in a previous communication (Carroll 1981). In this, micelles diffuse to the interface where they either dissociate and adsorb or simply diffuse away intact (for micelles, not being surface active, are not expected to adsorb as entities). Those that dissociate and adsorb (as monomers) trigger by their adsorption a concerted desorption from the interface, of an equivalent number of monomers in the form of micelles containing a certain quantity of the solubilizate. As only the diffusion of micelles *not* containing solubilized material to the oil-water interface is considered, and the model is pertinent only to initial rates, the experimental conditions described above are so arranged that it is this stage which is studied: after one droplet of oil has been completely solubilized the system is $<<1\%$ saturated.

The rate of solubilization can be written as the product of the flux, J_{out}, of micelles desorbing from the interface in unit time and the number of solubilizate molecules, b, carried by each of these micelles. J_{out} is related to J_{in}, the flux of micelles which actually adsorb, by the relation of $aJ_{out} = a_oJ_{in}$, where the number of monomers in the desorbing and adsorbing entities are respectively a and a_o. The flux J_{in} can be expressed in terms of a diffusion layer thickness Δ, of order of micelle size, the bulk micelle concentration $(c-c_o)/a_o$ (where c_o is the critical micelle concentration) and the fraction of micelles which dissociate while in the interfacial region, which depends on the micelle decay constant τ_2. J_{in} has the final form (Carroll 1981)

$$J_{in} = V_m \Delta(c-c_o)/a_o\tau_2,$$

so that J_{out} has the form

$$J_{out} = V_m \Delta(c-c_o)a\tau_2,$$

where V_m is the molar volume of the solubilizate.

In previous work it was assumed that the amount of solubilizate, b, associated with a desorbing micelle is proportional to the equilibrium solubilization capacity, with the same proportionality constant for different oils. However, this is not necessarily true: the quantity b calculated in this way may differ from the equilibrium quantity for two reasons; first, the aggregation number, and hence the b-value (Nakagawa et al 1960) of the desorbing micelle may differ from that of the fully equilibrated species and, second, the shape of the latter is certain to be quite different from the shape of the desorbing micelle at the stage where it parts company with the interface. The kinetic b is thus related to the equilibrium value b_s by a relation of the form $b = b_sG(p,q)H(s)$, where G is a function of the aggregate numbers a_o, a and a_s of the 'empty', desorbing and equilibrated micellar species ($p = a/a_o$; $q = a_s/a_o$) and H is a function of the shapes of the micelle at the desorption stage. The overall rate of the process, the flux of oil into solution, is thus

$$F = b_sG(p,q)H(s)J_{out} \quad (1)$$

which becomes on use of the relations $a_oJ_{in} = a\,J_{out}$ and $b_s = a_sB_s$, where B_s is the equilibrium capacity expressed in terms of molecules of oil per molecule of active,

$$F = \frac{a_oa_s}{a} B_sG(p,q)H(s)J_{in} \quad (2)$$

$$= F_s\frac{a_s}{a} G(p,q)H(s) = F_sG'(p,q)H(s) \quad (3)$$

where F_s is defined as the 'standard' flux prevailing when $a = a_s$, i.e. $F_s = a_oB_sJ_{in}$; and $G'(p,q) = (a_s/a)G(p,q)$. Thus under the conditions where the oil flux is F_s it is expected that for two oils the ratio of the measured rates should be in the ratio of the respective B_s values, or that the slopes of the lines in Fig. 3 be proportional to the quantity at the same temperature. The explanation for deviations from this rule lies in deviations of the product of the correction factors, $G'(p,q)H(s)$, from unity.

The experimentally determined ratio of the rates for hexadecane and HMT is about 16:1 and that for the B_s values is about 7·5:1, from which it is deduced that the ratio of the terms $G'(p,q)H(s)$ for the two oils must be about 2. In the Appendix, an estimate is made of $G'(p,q)$ for the case of spherical micelles and it is shown that this term alone could account for the factor 2 for reasonable combinations of the aggregation numbers of the micelle species present. The shape factor H is much more difficult to quantify, but an indication of its magnitude is provided by comparison of the B_s data obtained for the present micellar species with similar data for the uptake of the same two oils by planar black films of glyceryl mono-oleate reported by Gruen & Haydon (1980). Whereas in the present systems the ratio of hexadecane to HMT is about 7·5:1, in the latter systems this ratio is 25:1. It is therefore easy to believe that the factor H may differ appreciably from unity for a micelle forming at the oil/water interface.

The product of the two terms G and H, although probably never unity, is nevertheless not expected to alter the theoretical rate by as much as one order of magnitude. It is therefore possible, by using the expression already given for J_{in} and the various experimental data, to obtain an order of magnitude estimate of the quantity Δ, which is given by the expression

$$\Delta = \frac{2a\tau_2}{bV_m}\frac{dF}{dc} \quad (4)$$

The micelle relaxation time τ_2 has been estimated for this sytem by Lucassen (1975), using a dynamic surface tension method, to be 5×10^{-3}s. For hexadecane at 313K, dF/dc = 0·6 μm min^{-1} per 1% $C_{12}E_6$, a/b ≈ 1, and V_m = 294, which gives Δ = 15 nm, which is of the correct order of magnitude for the micelle dimensions, which, it is expected, Δ will reflect (Carroll 1981).

The linearity of the plots of rate against active concentration (Fig. 3), taken with the theoretical expression for the rate would indicate that the relaxation time τ_2 is independent of the active

concentration over the range studied, provided that all the other quantities are similarly independent of concentration. Although at variance with much of the literature on micelle dissociation, this result is consistent with the results of Herrmann & Kahlweit (1980) (on non-ionic active) and of Takeda et al (1977) (on ionic active). Both groups of authors showed that the relaxation time τ_2 is independent of active concentration except over a narrow concentration range close to the cmc. The latter range is too small to affect the results reported in the present work. Takeda et al worked with a highly purified sample of an anionic active and showed that the form of concentration dependence commonly reported in the literature could in fact be induced in their system by the addition of small quantities of active homologues with the principal component but of shorter or longer alkyl chain length. This suggests that such substances, which are a common kind of impurity in surfactants, may be responsible for much of the reported behaviour. In the present work pains were taken to establish the absence of such contaminants: purity was checked by g.l.c. and also by the absence of a minimum at the c.m.c. in the surface tension isotherm. The latter test is traditionally regarded as a stringent criterion for surface chemical purity, it being especially sensitive to the presence of small quantities of active more strongly adsorbed at the interface than the principal component. It is rather surprising therefore, to note that in the literature on micelle dissociation this test is nowhere applied, although the sensitivity of τ_2 to trace contaminants has been remarked on (e.g. Hoffmann et al (1976)).

The temperature dependence of the solubilization rates for n-hexadecane and HMT is qualitatively the same as that reported for the system C_8E_4/HMT (Carroll 1981) in that the rate increases with temperature and very rapidly so as the cloud point is approached. The Arrhenius plots are given in Fig. 5. These plots are sensibly linear over the range given and can both be fitted with straight lines of the same gradient, corresponding to an activation energy of $\approx$125 kJ mole^{-1}. Activation energies of this magnitude have been reported for micelle dissociation involving C_{12} actives by others (see e.g. Hoffmann et al 1976). The independence of the reported energy on the oil type is consistent with the idea that the rate-determining stage does not involve the solubilizate: a conclusion which is in accord with the proposed mechanism. In the above, the contributions of other temperature-dependent processes (involving Δ or b/a, for example) have been ignored because no quantitative data are available. Consideration of the likely magnitudes of these contributions suggests that these are unlikely to exceed 20% of the total activation energy.

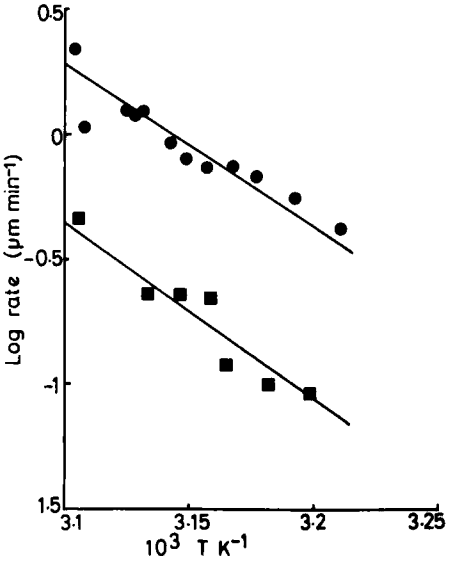

FIG. 5. Arrhenius plots for data of Fig. 4. Hexadecane (●) HMT (■).

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APPENDIX

The correction factor G(p,q) for micelle aggregation number variation

Let the aggregation number of the 'empty' micelle be a_o, that of the desorbing micelle be a and that of the fully equilibriated micelle be a_s. If α is the area per head group of active in the micelle, the surface area of the micelle is αa_o for 'empty' (adsorbing) micelles, with similar expressions for the other two cases. The micelle volume is thus $ka_o^{3/2}$ (or $ka^{3/2}$, or $ka_o^{3/2}$) in the case of spherical micelles. If it is assumed that the amount of oil, b, associated with a micelle is related to the difference in volume between this and the 'empty' micelle, then

$$b = k'(a^{3/2} - a_o^{3/2}) \qquad (A1)$$

If b_s refers to the saturation value of b ($a = a_s$), it is clear that

$$b = b_s(a^{3/2} - a_o^{3/2})/(a_s^{3/2} - a_o^{3/2}), \qquad (A2)$$

$$= b_s(p^{3/2} - 1)/(q^{3/2} - 1), \qquad (A3)$$

where $p = a/a_o$ and $q = a_s/a_o$. The factor G(p,q) introduced in the discussion section is evidently the coefficient of b_s in eq (A3). Likewise, the factor G'(p,q) introduced in the last section has the form

$$G'(p,q) = \frac{q}{p}\,\frac{p^{3/2}-1}{q^{3/2}-1} = \frac{p^{1/2}-p^{-1}}{q^{1/2}-q^{-1}} \qquad (A4)$$

The ratio of these factors for two oils is thus

$$\frac{G'_1}{G'_2} = \left(\frac{p_1^{1/2}-p_1^{-1}}{p_2^{1/2}-p_2^{-1}}\right)\left(\frac{q_2^{1/2}-q_2^{-1}}{q_1^{1/2}-q_1^{-1}}\right) \qquad (A5)$$

The function $x^{1/2} - x^{-1}$ is easily tabulated for a series of values of x(= p or q) in the range pertinent to the problem (say x = 1 to 5). The parameter a_o is the same for both oils so that corresponding values of a and a_s are readily evaluated.

Given the conditions $a_o^1 = a_o^2$, $a_s^1 > a_s^2$ and $a^1 > a^2$, it is possible to obtain ratios greater than unity from eqn (A5) in two ways, which are respectively when $a_o < a < a_s$ and when $a_o < a_s < a$. In the former case $G' < 1$; in the latter case $G' > 1$. In the latter case supersaturation of the micelles occurs. (This occurrence and subsequent events have been recently discussed by Tondre & Zana (1980).) Examples of the two possible cases are provided by the sets of values $a_o = 300$; hexadecane: $a = 507$, $a_s = 675$; HMT: $a = 363$, $a_s = 507$ and $a_o = 300$; hexadecane: $a = 1200$, $a_s = 507$; HMT: $a = 507$, $a_s = 432$: both sets of figures result in a ratio of about 1·8:1 for the two G' factors.

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