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EVIDENCE FOR THE SEQUENTIAL SELF-ASSOCIATION MODEL IN REVERSED MICELLES

Charmian J. O'Connor* and Terence D. Lomax
Chemistry Department, University of Auckland, Private Bag,
Auckland, New Zealand.

Abstract: Application of the sequential self-association model to aminolysis reactions in alkyldiamine bis(dodecanoate)-benzene systems is investigated.

Surfactant association in apolar solvents is predominantly the consequence of dipole-dipole and ion pair interactions between the amphiphiles. This is quite different from the Hartley model[1] of opposing hydrophobic attractions and electrostatic repulsions which are responsible for micellization in water, and kinetic treatments dependent upon a monomer $\rightleftharpoons$ *n*-mer equilibrium may not necessarily be applicable to those in apolar solvents.

Several studies[2,3] have been made on the decomposition of *p*-nitrophenylacetate, PNPA, in the presence of alkylammonium carboxylate surfactants in apolar solvents. The products of decomposition are *p*-nitrophenol and the corresponding amide and even in the presence of a large excess of cosolubilized water no products of hydrolysis have been detected.

In apolar media, surfactants whose average aggregation number is less than four show changes in physical properties which are gradual,[2,4,5] and such data cannot be described by a monomer $\rightleftharpoons$ *n*-mer type equilibrium. In 1975 Lo *et al.*[6] described such gradual physical changes in terms of a sequential type self-association model, Scheme I. If all values of the equilibrium constants K_{12}, K_{23}, ------, K_{ij} are assumed to be equal, then the weight fraction of the monomer, f, is related to the stoichiometric concentration of detergent, [D], by Eq. 1.[7]

Scheme I

$$\text{monomer} + \text{monomer} \xrightleftharpoons{K_{12}} \text{dimer}$$

$$\text{dimer} + \text{monomer} \xrightleftharpoons{K_{23}} \text{trimer}$$

$$(n\text{-}1)\text{-mer} + \text{monomer} \xrightleftharpoons{K_{ij}} n\text{-mer}$$

$$(1-f^{\frac{1}{2}})/f = K_{ij}[\mathrm{D}] \qquad (1)$$

If we set K_{ij} equal to 100 (this arbitrary value was chosen because it lies within the range 50-300 obtained for alkylamine salts in non-polar solvents[6,8]) we can calculate the fraction of dimer, trimer, *etc.*, present in such a surfactant system.

Our recent studies have included the rate of aminolysis of *p*-nitrophenylacetate, PNPA, in a series of α,ω-diamine bis(dodecanoate) surfactants dissolved in benzene. A plot of the pseudo second order rate constant, $k_\psi/[D]$, for aminolysis of PNPA in butane-1,4-diamine bis(dodecanoate) is shown in Figure 1. Similar profiles were obtained for each surfactant in the series whose diamine carbon chain length increased from 2 to 12 carbon atoms.

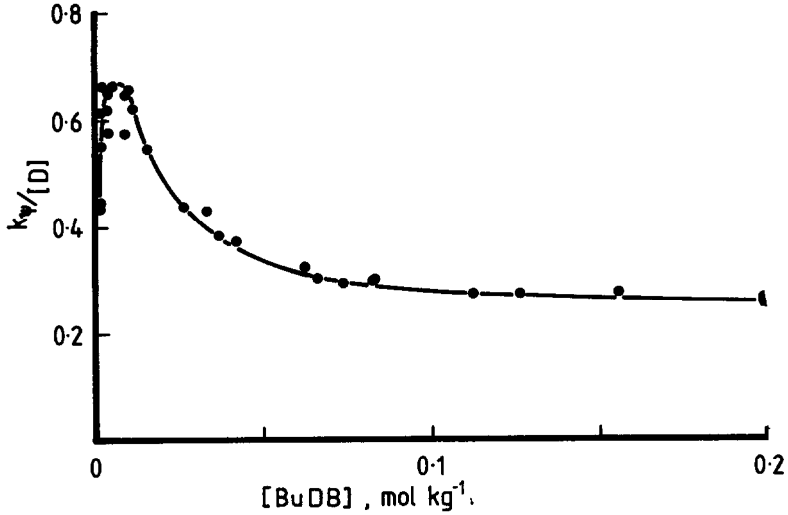

Figure 1 Plot of pseudo second order rate constant, $k_\psi/[D]$, against [D], showing the distorted bell-shaped profile followed by a plateau for the aminolysis of *p*-nitrophenylacetate by butane-1,4-diamine bis(dodecanoate) in benzene at 341 K.

If we postulate that the observed rate constant includes equal contributions from all the aggregates present in solution, as well as from the monomeric detergent, the kinetic results may be represented by Eq. 2:

$$\frac{k_\psi}{[D]} = \frac{k_1[\text{monomer}]^2}{[D]} + \frac{k_2[\text{dimer}]}{[D]} + \frac{k_3[\text{trimer}]}{[D]} + \cdots\cdots + \frac{k_n[n\text{-mer}]}{[D]} \tag{2}$$

Substitution of Eq. 3, an arbitrary but useful allowance for monomer contribution, into

$$k_1 \;[\text{monomer}]^2 = k_2 \;[\text{dimer}] \tag{3}$$

Eq. 2 leads to the supposition that $k_\psi/[D]$ should be proportional to ([total aggregate] + k_2 [dimer]).

Plots of fraction of total aggregate, ([total aggregate]/[D]), against [D] and of ([total aggregate] + k_2[dimer])/[D] against [D] are shown in Figure 2 for K_{ij} = 100. It is seen that the upper profile, in which allowance is made for contribution from the monomer and all oligomers, closely resembles that obtained from the kinetic results, Figure 1. This result suggests that the self aggregation model, Scheme I, may better explain the observed kinetics in these systems than does the pseudo phase model which allows for only one aggregational state and for which the monomer is normally regarded as an unreactive species.

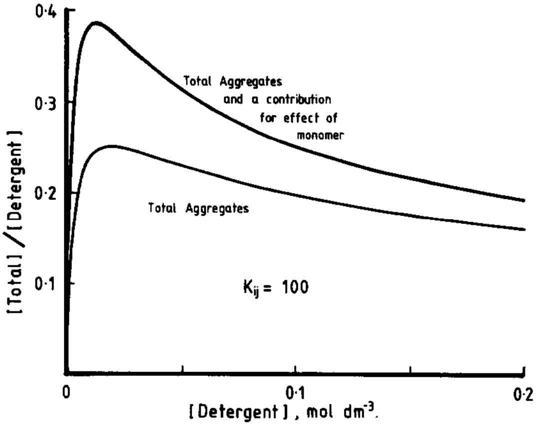

Figure 2 Plots of fraction of total aggregate, lower plot, and of total aggregate plus a contribution for the effect of monomer, upper plot, against [detergent] for K_{ij} = 100.

We have additional evidence to suggest that the aminolysis of esters by surfactants in apolar solvents is not a micellar phenomenon. If it were, then the addition of water, which is known to increase both the aggregate size and the aggregation number to form a more micelle-like structure should result in an increase in rate. But we found^3 that the rate decreased quite rapidly, approaching that in aqueous medium as the concentration of cosolubilized water

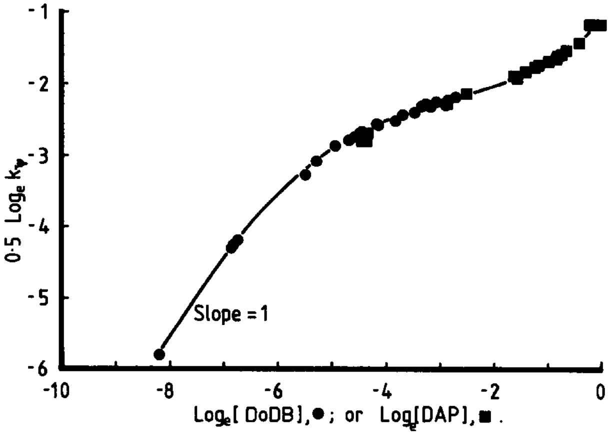

Figure 3 Plots of 0.5 $\log_e k_\psi$ against $\log_e$[D] for ●, dodecane-1,12-diamine bis(dodecanoate), DoDB, and ■, dodecylammonium propionate, DAP. Note also the upwards curvature as the fraction of monomer, f, in solution increases.

was increased. Physical evidence also supports the non-micellar behaviour of such systems for there is no abrupt change in physical properties with increasing surfactant concentration to which one can assign a meaningful value of CMC.

Moreover we find that as the concentration of detergent is increased, the linear dependence of rate upon [D], which is observed at moderate [D], no longer exists and that the rate profile bends upwards at high [D]. Similar non-linear dependence at high dodecylammonium propionate concentration has been observed[9] for decomposition of *p*-nitrophenylcarbonate.

The value of K_{ij} in Eq. 1 is inversely proportional to the dielectric constant of the medium, which in turn is a function of both the dielectric constant of the solvent and of the detergent. As [D] increases, the dielectric constant of the medium and thereby the value for the weight fraction of the monomer also increase. If we postulate that the contribution of the monomer to the overall kinetics is equal to, or greater than, those of the oligomeric species, then at high [D], when f increases, the dependence of k_ψ upon [D] once again approaches second order. However at moderate [D], formation of oligomers tends to remove monomer from the solution and values of k_ψ, which become more nearly dependent upon [D], reflect this association.

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