Kinetic Studies of Alcohol–Surfactant Mixed Micelles

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1 Introduction

Surfactants or surface-active agents are amphiphilic and, because of this characteristic, they are widely used in industrial applications to stabilize dispersions such as foams, emulsions, and suspensions. Of equal significance is the fact that monomer surfactant species self-aggregate at the critical micelle concentration (cmc) to form large aggregates called micelles. The properties of micelles depend upon parameters such as temperature, pressure, concentration, and the chemical nature of the surfactant. Both charged (anionic and cationic) and neutral micelles can be formed. In the case of the former, the degree of association of the counterions around the charged head groups of the micelle makes an important contribution to the factors that stabilize the micellar aggregates.

The effect of alcohol additives on the thermodynamic properties of micellization[1–3] and the structure of micelles[4–7] has been widely studied. Particular attention has been focused on alcohols because, by varying the hydrocarbon chain length in a systematic manner, one can distinguish between mixed micellar systems in which the alcohol either partitions between the micellar and bulk phases or penetrates the micelles. As the alcohol concentration and hydrocarbon chain length increase, the mixed micelles gradually break down and the alcohol can then exist as microscopic droplets in which the surfactant species now acts as a surface-active agent that solubilizes the alcohol droplets within the aqueous environment. In these cases the relative hydrophobicity of the surfactant and cosurfactant becomes an important factor in governing the onset of such behaviour.

There appears to be evidence from industrial applications that some mixed aggregate systems of surfactant and cosurfactant yield better results than mixtures of surfactants.[8] From an economic viewpoint this is important as less costly cosurfactant components, such as alcohols, may be used to replace more costly surfactant components.

The study of kinetic processes in mixed aggregate systems is an important aspect of understanding the factors that govern the creation, growth, and dissolution of aggregates. The object of this review is to give non-specialists an understanding of two fast kinetic techniques that are used to obtain information about the dynamic processes in micellar aggregates and to summarize the results of recent kinetic studies associated with the exchange of surfactant and alcohol species between mixed micelles and the bulk phase. It will be shown that fast relaxation techniques using ultrasonic sound absorption can provide information about these rapid exchange processes. The slower relaxation process of micelle formation and dissolution, observed by T-jump measurements, will also be qualitatively discussed.

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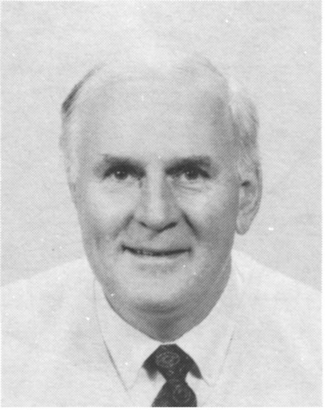

2 Principle of Chemical Relaxation

Chemical relaxation techniques are used to study the kinetics of fast chemical reactions in solution. The principle of chemical relaxation techniques, such as ultrasonic absorption and temperature-jump (T-jump) methods, can be briefly described as follows. A chemical system or reaction at equilibrium is perturbed by creating a rapid but very small change of one of the external parameters that determines the system's equilibrium state. This results in a shift of the system to a new equilibrium determined by the final value of the parameter that was perturbed. As the system relaxes from the old to the new equilibrium condition, its evolution can be characterized by one or (more) time constant(s), the so-called relaxation time(s). Consequently, the relaxation times reflect the ability of a system to follow the perturbation and, hence, they are dependent on the rate constants of the chemical reactions being studied. A small perturbation (first order, linear) ensures that the system remains close to equilibrium and that the kinetics of the relaxation to the new equilibrium position takes on a rather simple mathematical form. It is important to realize that relaxation times are macroscopic properties of the system and the difficulty of interpreting experimental data is to relate these macroscopic times to those relaxation times which characterize molecular processes in the system.

3 Experimental Methods

The intent of this section is to provide some basic understanding about the T-jump and ultrasonic sound absorption methodologies, the two key techniques that have been used to obtain experimental data which will be discussed in Sections 5 and 6.

3.1 T-jump

There are various ways in which the system's initial equilibrium condition can be disturbed. If the chemical reaction has a non-zero ΔH°, then a common technique is to increase the temperature rapidly, usually by the rapid discharge of a capacitor[9] or heating by a pulse of laser light of appropriate wavelength.[10] The use of a discharge across electrodes placed in a conducting solution gives rise to quick, ohmic heating which can raise the temperature of a tiny cell containing a reaction mixture by $1 \sim 2$ degrees in $< 10^{-7}$s. One can monitor conductivity, if there are changes in the concentration of charged species in solution, or light absorption changes at a suitable wavelength, if there is an intrinsic chromophore in the system or there is a small quantity of an added chromophore, to follow the rate of re-equilibrium. Spectrophotometric detection in the case of micelle systems implies that a chromophore-containing surfactant has a spectrum that is strongly dependent on whether it is free or micellized. Since few surfactant molecules contain a chromophore, an added dye whose spectrum depends on whether it is associated with the micelle can be used to study the kinetics of micelle formation–breakdown. When using this method, it is important to keep the molar ratio of surfactant to dye very large so that the introduction of dye molecules does not disturb the structure of the micelles.

3.2 Sound Absorption

Another type of chemical relaxation technique makes use of high frequency sound waves. An ultrasonic wave is primarily an oscillating pressure. But it is also an oscillating temperature because the propagation of sound waves through an elastic medium occurs almost adiabatically. The absorption of sound by a medium is a consequence of various irreversible, essentially frictional processes that take place during the compression–rarefaction cycles that occur as a sound wave passes through the solution.[11,12] If a chemical reaction system that has non-zero values of ΔH° and/or ΔV° is present, then the equilibrium position can be cyclically perturbed by the sound wave with the frequency of the sound wave. If the rate of reaction is slow compared to the sound frequency, then the reacting system cannot follow the changing equilibrium constant, and the solution behaves as though it were unreactive, *i.e.*, only classical sound absorption due to frictional effects prevail. However, if the reaction rate is fast compared to the sound frequency, then the reacting system follows the changing equilibrium position. The net result is that there is absorption of energy from the sound wave to supply heat to the reaction; the sound absorption coefficient, α is thereby increased.

One way to generate sound waves is as follows. An electric field is applied in the direction of a polar axis in a quartz crystal; this is the converse of the piezoelectric effect. The crystal is mechanically strained and the degree of strain is proportional to the applied field. However, only pulses of ultrasound of frequency f corresponding to the odd harmonics can be generated because of the polarized nature of the piezoelectric effect.[13] Generally, one can obtain experimental sound absorption data to at least the 12th odd harmonic mode of the fundamental frequency of the crystal. In our work we have used X-cut quartz crystals with fundamental frequencies of 5 and 10 MHz and this permits measurements in the range of 5 to 230 MHz.

3.2.1 Ultrasonic Absorption Techniques

Two ultrasonic absorption techniques are currently in use: the versatile, pulse technique[9] and a sweep frequency acoustic cavity resonator technique.[14–16] In the pulse apparatus two parallel X-cut quartz (piezoelectric) crystal plates are immersed in a solution to be studied. One of the crystals is fixed while the second is attached to the end of the shaft of a precision micrometer, thus enabling the path length between the crystals to be varied. One crystal sends pulses of ultrasound of frequency f through the solution, where they are attenuated before reaching the second crystal (receiver). The attenuation is measured as a function of the distance separating the crystals using a comparison method. The absorption of ultrasound coefficient, α, is obtained from a plot of attenuation *versus* distance at a frequency f.

The cavity resonator consists of a cell having two matched X-cut quartz crystals with the liquid sample, typically only a few mL, introduced between them. Ultrasonic absorption measurements at frequencies around and below 1–2 MHz had been troublesome, with respect to the liquid quantities required and the accuracy obtainable, prior to the introduction of this technique.[14,15] The transmitting crystal is continuously excited with a high stability frequency synthesizer over a predetermined bandwidth. The resulting sound waves produced in the systems are detected by the receiving crystal and recorded as voltage *versus* frequency. When conditions are such that the path length of the resonator is an integral number of half-wavelengths of the propagating wave, the cell resonates and the output voltage of the receiver crystal goes through sharp maxima at definite frequency intervals. The latter depend on the path length of the cell and the acoustic properties of the liquid.

If the ultrasonic absorption measurements could be performed with an ideal resonator containing only the energy loss due to the solution, then the ultrasonic absorption per wavelength, $\alpha\lambda$, in the liquid would be given by

$$\frac{\alpha\lambda}{\pi} = \frac{\Delta f_n}{f_n} = \frac{1}{Q} \qquad (1)$$

where Δf_n and f_n are the half power bandwidths and frequency, respectively, of a resonant peak, λ is the wavelength, and Q is the quality factor of the resonator. In practice the measured quality factor, Q_T, is related to that of the solution, Q_S, and the mechanical quality factor, Q_M, as shown in equation 2.

$$Q_T^{-1} = Q_S^{-1} Q_M^{-1} \qquad (2)$$

The term Q_M^{-1} includes losses arising from effects due to the beam divergence and incomplete reflection of the sound wave at the quartz surface. Q_M^{-1} can be eliminated by performing a measurement in the same cell at the same frequencies with a reference liquid which has acoustic properties similar to the solution. The excess absorption per wavelength, $\alpha\lambda_{excess}$, in the solution is obtained from equation 3.

$$\alpha\lambda_{excess} = \pi[(\Delta f_L - \Delta f_R)/f_n] \qquad (3)$$

where Δf_L and Δf_R are the corresponding half power bandwidths of the *n*-th resonance peak in the solution and reference liquid, respectively. A more complete description of the resonators and the theory is given elsewhere.[16]

3.2.2 General Equation for Ultrasonic Relaxation

It can be shown[9,11,12] that the variation of α with its frequency, f, has an inflection point at the frequency equal to $1/\tau$, where τ is the relaxation time. Figure 1 shows the dependence of α/f^2 on frequency in an experimentally ideal situation. The relaxation time is expressed in terms of the relaxation frequency, f_r,

$$\tau^{-1} = 2\pi f_r \qquad (4)$$

and the expression relating α/f^2 to frequency is written as

$$\alpha/f^2 = A[1 + (f/f_r)^2] + B \qquad (5)$$

where A is the amplitude of the relaxation, f_r is the relaxation frequency, and B measures the contribution from frictional

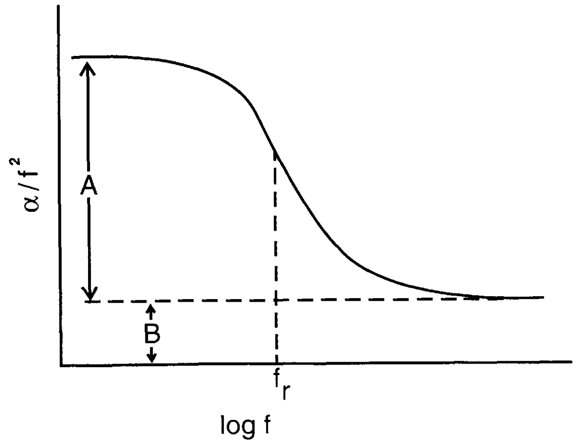

Figure 1 Graphical representation of dependence of α/f^2 on frequency for a system having a single relaxation frequency, f_r.

processes, *e g* , shear viscosity, and also can include a/f^2 arising from other processes having relaxation frequencies at much higher frequencies than f_r in equation 5 In the case where there may be more than one observed relaxation process, then the first term on the right-hand side of equation 5 is replaced by a summation of terms Ultrasonic relaxation studies of some systems are often limited by the difficulty of resolving two relaxation processes separated by a small factor It will be shown later that some moderate success has been achieved in studying systems of surfactants and alcohols where relaxation times are separated by a factor as low as five

4 Micellar Dynamics

Prior to 1970, there was some disagreement among workers concerning the origin and characteristics of the relaxation processes in regular micelle systems [17] Two well-separated relaxation times were observed On the one hand, T-jump and P-jump experiments consistently revealed the existence of a single relaxation process with relaxation times in the range $10\ ^{2}$ $10\ ^{4}$ s On the other hand, ultrasonic absorption studies showed the existence of a relaxation process in the range of $10\ ^{7}$–10^{-10} s

In 1974, a theoretical treatment of the kinetics of neutral micelles of one component was reported by Aniansson and Wall[18] and it led the way to general agreement among workers concerning the assignment of these chemical relaxations to specific equilibrium processes The fast relaxation time in the range below $10\ ^{6}$ s is associated with the dynamic equilibrium involving the partitioning of the monomer surfactant species between the bulk and the micellar phase The other, relatively slower, relaxation process is associated with the dissolution–formation of the micelle It was later shown[19 20] that taking account of counterions (ionic surfactant) only brought about a quantitative change while the qualitative picture remained unchanged

4.1 Mixed Micellar Systems

4 1 1 Fast Exchange Process

In 1979, Aniansson applied the basic ideas for a one-component non-ionic system to two-component systems [21] The theory predicts the existence of two fast relaxation processes as shown below for a mixed micelle (S_nA_a), containing neutral surfactant (S) and alcohol (A)

$$\mathrm{A} + \mathrm{S}_n\mathrm{A}_{a\ \ 1} \underset{k_2}{\overset{k}{\leftrightarrows}} \mathrm{S}_n\mathrm{A}_a \underset{k_1}{\overset{k}{\rightleftarrows}} \mathrm{S}_{n\ \ 1}\mathrm{A}_a + \mathrm{S} \qquad (6)$$

where k_1^+ and k_1 are the forward and backward rate constants, respectively, for the exchange of surfactant with the mixed micelle and k_2^+ and k_2 are the forward and backward rate constants, respectively, for the exchange process of the alcohol with the mixed micelle

Equations 7 and 8 are the relations derived by Aniansson[21] which link the relaxation times to kinetic constants and other system parameters

$$1/\tau_{1\ \mathrm{S}} = k_1\ /\sigma_\mathrm{S}^2[1 + \sigma_\mathrm{S}^2C_\mathrm{m}/\mathrm{cmc} - \sigma_\mathrm{A}^2\sigma_\mathrm{S}^2/\sigma_\mathrm{AS}^4(1 + \sigma_\mathrm{A}^2C_\mathrm{m}/C_\mathrm{A}^\mathrm{f})\ \ ^1] \qquad (7)$$

$$1/\tau_{1\ \mathrm{A}} = k_2\ /\sigma_\mathrm{A}^2[1 + \sigma_\mathrm{A}^2C_\mathrm{m}/C_\mathrm{A}^\mathrm{f}] \qquad (8)$$

where σ_A^2 and σ_S^2 are the variances in the mean alcohol aggregation number (a) and the mean surfactant aggregation number (n), respectively, σ_AS is a measure of the correlation (or covariance) between σ_A^2 and σ_S^2, C_A^f is the concentration of alcohol not micellized, cmc is the critical micelle concentration in the presence of the alcohol, and C_m is the concentration of micelles, given by

$$C_\mathrm{m} = (C_\mathrm{S} - \mathrm{cmc})/\bar{n} \qquad (9)$$

where C_S is the total surfactant concentration

In 1981, Hall[20] showed that the previous treatments of micellization kinetics required modification to allow for changes in rate constants with solution composition These changes arise from factors responsible for non-ideal behaviour and, for ionic micellar systems, from micelle–counterion interactions His theory was also applicable to micelles of more than one component and to solutions which contain other additives such as alcohols Although the theory does involve approximations, it is noteworthy that for solutions of neutral surfactants these approximations lead to expressions for the fast relaxation process of single component micelles obtained previously [18]

The relatively more complex expressions developed by Hall will not be given here Suffice it to say that a key experimental parameter in considering the effect of charged ions on the rate constant(s) of the fast exchange process(es) for solutions of a single ionic surfactant or of mixed micelles of ionic and non-ionic components is the degree of micellar dissociation This property can be estimated from specific or equivalent conductance measurements [22]

4 1 2 Slow Process of Micelle Formation–Breakdown

In the first attempt to develop a theoretical interpretation of the slow process,[18] it was assumed that the micelle formation–breakdown occurred through a series of stepwise reactions

$$\mathrm{S}_n + \mathrm{S} \rightleftarrows \mathrm{S}_{n+1} \qquad (10)$$

one monomer, S, at a time associates with, or dissociates from, an aggregate, S_n Reactions between aggregates S_n and S_n, shown in equation 11, were not considered to be important

$$\mathrm{S}_n + \mathrm{S}_n \rightleftarrows \mathrm{S}_{n+n} \qquad (11)$$

This model of micellar solutions at concentrations just above the cmc was based on thermodynamic calculations of the aggregate size distribution and the subsequent modification of the curve following a very rapid perturbation The curve, represented as a plot of $\bar{S}_n$, equilibrium concentration of S_n, against n shows essentially three regions The first consists of monomers and small aggregates such as dimers, trimers, *etc* The second region, a minimum, refers to intermediate aggregates The third region, a maximum, refers to micelles proper and the value of n for which the maximum occurs is very close to the values measured by classical methods The minimum (second region) between the oligomers, *i e* , $n = 1, 2,$, and the proper micelles is responsible for the two relaxation processes in micellar systems Rapid perturbation of the system causes the proper micelles and monomers or oligomers to equilibrate, quickly, according to equation 10 However, this is a quasi-equilibrium state, as the rapid gain or loss (exchange process) of a small number of monomers does not allow oligomers and micelles to reach equilibrium during the rapid exchange The slow process is concerned with the approach to a final equilibrium of the system, *i e* , a further adjustment in the distribution curve This equilibration involves many steps such as equation 10 and also involves the concentration of species at the minimum in the size distribution curve The large number of steps involved gives rise to the longer time for τ_2 and the depth of the minimum determines the rate of micelle formation–breakdown

An expression for τ_2 for a single non-ionic surfactant was obtained [18] More complex expressions for ionic surfactants[19 20] and an extension of the theory to include reactions between submicellar aggregates, equation 11, at higher surfactant concentrations[19] were also developed For the latter situation the expression for τ_2^{-1} becomes

$$\tau_2\ ^1 = \tau_{21}^{-1} + \tau_{22}^{-1} \qquad (12)$$

where τ_{21} and τ_{22} refer to the contributions arising from equations 10 and 11, respectively. The terms add as though they were parallel resistances, in keeping with the analogy that passage through the minimum in the aggregate size distribution curve is similar to a resistance that opposes the transfer of monomers between oligomers and regular micelles. Equation 12 is applicable in systems where the intermicellar interactions are not too repulsive, *e.g.*, non-ionic surfactants and ionic surfactants at high ionic strength or in the presence of high charge density counterions. Extension of the general theory to include two-component surfactant systems have been proposed.[20,23] Rather complex relationships for τ_2 arise and there have been very few attempts to conduct a quantitative analysis of τ_2 data for mixed micellar systems in terms of these.

5 Micellization Kinetics of Fast Exchange Processes in Mixed Alcohol and Ionic Surfactant Systems

Experimental results obtained from ultrasonic absorption studies for the fast exchange processes in these systems clearly differentiate between two classes of systems. While the theory predicts the existence of two fast relaxation processes, in the case where the alkyl chain length of the surfactant is very long, C_{12} or longer, only a single relaxation is observed which is associated with the rapid exchange of the alcohol species from the mixed micelle. This occurs because the long alkyl chain of the surfactant pushes the relaxation time for the surfactant to longer values, *i.e.*, outside the time scale that can be studied by ultrasonic absorption techniques, although it still is possible to measure it using a shock-tube (P-jump) apparatus.

5.1 Alcohol Exchange between Mixed Micelles of Short to Medium Chain Length Alcohols and Long Chain Length Surfactant and the Bulk Phase

Ultrasonic studies of the solubilization kinetics of mixed micelles for the exchange of aliphatic alcohols containing four to six carbon atoms with surfactants having fourteen or more carbon atoms have been most extensively studied.[24–26] A Langmuir-type kinetic model for the adsorption–desorption of the alcohol at the micelle surface was first used to treat the data[26] but was later shown[24,27] to be inappropriate. The rate constants were assumed not to depend on solution composition.

However, Aniansson's theoretical treatment of mixed micelles,[21] equations 7 and 8, has shown that quantitative estimates of k_2^- and k_1^- can be obtained only if the equilibrium properties of mixed micelles (composition and mean aggregation numbers) and concentration of free surfactant are known. In some of the early work,[24,26] data used to estimate equilibrium concentrations of alcohols in the aqueous phase were confined mainly to solutions saturated with alcohol and provided no direct information about the unsaturated solutions studied in the experiments using ultrasonic techniques. Improved quantitative studies of the partitioning of the alcohol between the bulk aqueous phase and the micelles, using the head space analysis method involving gas chromatography, were obtained[27,28] for similar composition conditions of the components as those used in the ultrasonic measurements. The results for systems of pentanol with hexadecylpyridinium chloride (HDPC),[27] of 2-butoxyethanol (BE) with tetradecyltrimethylammonium bromide (TTAB) and hexadecyltrimethylammonium bromide (CTAB),[29] and of pentanol with sodium dodecylbenzenesulfonate (NaDBS)[28] indicated that the amount of micelle solubilized alcohol increases, linearly, as a function of total alcohol concentration.

Table 1 Values of exit rate constant of alcohol from alcohol–surfactant mixed micelles

Surfactant	Alcohol	$k_2^-(s^{-1})$ × $10^{-7,e}$	× 10^{-9}
SDS	n-C_5	1.9[a]	
NaDBS	n-C_5	1.3[b]	
TTAB	n-C_5		~1[d]
	BE	2.0[b]	
CTAB	n-C_3	8.1[c]	
	n-C_4	5.8[c]	
	n-C_5	2.6[c]	
	n-C_6	0.9[c]	
	BE	4.8[b]	

[a] From *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 1674. [b] From ref. 28. [c] From ref. 26. [d] From ref. 24. [e] Phenomenological model used by authors corresponds to $k_2^-/\bar{n}$.

Using a phenomenological treatment[20] to evaluate the micellization kinetics of the alcohol exchange, the magnitude of k_2^- was observed to increase with increasing alcohol content. Estimated values of k_2^- obtained for conditions where the total alcohol concentration approaches infinite dilution or is a representative value of the low alcohol concentration range are shown in Table 1. It appears that in the case of data derived from the phenomenological model the value of k_2^- should correspond to $k_2^-/\bar{n}$. Although only a few alcohols have been used in these studies, there are qualitative features of the data that provide some insight into the relative importance of the factors that control the kinetics of the alcohol exchange.

In the case of pentanol, for which there are data for mixed micelles containing four different surfactants, there appears to be little dependence (within experimental error) of k_2^- on the charged nature of the head group of the surfactant (anionic or cationic) or on the type of counterion. If these factors do play a role, then studies with a wider selection of head groups and counterions as well as improved accuracy in the experimental determination of k_2^- will be required to make such an unequivocal determination.

A clearer picture of the dependence of k_2^- on the alkyl chain length of the alcohol is evident. In the case of the results for the series of alcohols with CTAB, the estimated values of k_2^- are seen to increase as the hydrocarbon chain length of the alcohol decreases. This is consistent with the qualitative picture for these mixed aggregates that the hydrophilic head of the alcohol locates, approximately, in the micelle head group region while the hydrophobic tail embeds itself in the interior of the micelle. Here, the hydrocarbon chain of the alcohol can interact, hydrophobically, with the hydrocarbon chains of the surfactant. An increase in the alcohol chain length increases the hydrophobic interactions, thus leading to increased stabilization of the alcohol in the mixed micelle and a reduction in the exit rate of the alcohol.

A subtle feature of incorporating an ethylene oxide (EO) unit, CH_2-CH_2-O, into a normal alcohol chain is somewhat evident in these results. Rather than reducing the magnitude of k_2^-, as might be expected from an apparent lengthening of the hydrophobic part of the alkyl chain of the alcohol, it appears that BE behaves somewhat like a normal C_4 or C_5 alcohol when it is in a mixed micelle containing the same surfactant. This suggests that only the n-butyl segment of BE is embedded in the hydrophobic micellar core region. The unusual behaviour of the EO unit in these systems will be discussed in more detail in Section 5.3.

Corresponding values of k_2^+ can be obtained from the partition coefficient of the alcohol between the micellar and bulk phases, *i.e.*, $k_2^+ = Kk_2^-$. Invariably these values are of the order of 10^{10} $M^{-1}s^{-1}$ which indicates, not unexpectedly, a diffusion-controlled association of alcohol to the micelle.

5.2 Alcohol and Surfactant Exchange between Mixed Micelles of Medium Chain Length Alcohols and Long Chain Length Surfactant and the Bulk Phase

One of the first comprehensive studies of these systems was carried out by Yiv *et al.*[24] using P-jump and ultrasonic absorption techniques to measure τ_1 for the surfactant and alcohol, respectively Mixed micelle systems consisting of TTAB or CTAB with the series of alcohols, n-butanol to n-hexanol, were studied Having previously determined the composition and mean aggregation numbers of the mixed micelles and the concentration of free surfactant, they were able to analyse the τ_1 data in terms of equations 7 and 8 to obtain estimates of rate constants for the fast exchange processes The most extensive results were obtained for the TTAB–n-pentanol system at low alcohol concentrations A semi-quantitative approach was used to account for a decrease in the partition coefficient of the alcohol with increasing concentration, owing to the increased activity of the micellized alcohol

A value of about 10^9 s^{-1} (Table 1) was estimated for k_2^- of pentanol The corresponding value of k_2^+ was obtained from the partition coefficient of the alcohol, *i e*, $k_2^+ = Kk_2^- \cong 6 \times 10^9$ $M^{-1}s^{-1}$ The average residence time of an alcohol in the mixed TTAB–alcohol micelles, $T_R = \frac{\bar{a}}{k_2^-}$, was found to be *ca* 5×10^{-8} s Quantitative analysis of τ_1 for the other alcohols was not possible because the experimental measurements required to determine the extensive complementary equilibrium properties of the mixed micelles were not carried out

The exchange of surfactant between mixed micelles and surrounding solution was studied using a shock tube apparatus with conductivity detection However, because of experimental constraints, the detection was limited to a range of surfactant concentration from slightly above the cmc to ~3–4 cmc, and to a temperature of 5 °C This is in contradistinction to the ultrasonic absorption measurements which were obtained at 25 °C and over a wider surfactant concentration range Nevertheless, important qualitative characteristics of the effect of alcohol on τ_1 of the surfactant were identified

Values of τ_1^{-1} of TTAB and CTAB were observed to increase with alcohol concentration in experiments where the surfactant concentration remained constant This result is due to the effect of alcohol on the degree of micelle ionization, cmc and variance, σ_S (see equation 7) However, preliminary results concerning the effect of longer chain alcohols such as n-heptanol and n-octanol on τ_1 of TTAB showed that a more complex change occurs between n-hexanol and n-octanol On the one hand, for heptanol the curve for τ_1^{-1} *versus* alcohol concentration goes through a maximum at low heptanol concentrations and then decreases sharply A decrease of τ_1^{-1} with alcohol concentration was observed in the case of octanol In experiments where the alcohol concentration was kept constant, τ_1^{-1} increased linearly with surfactant concentration, as in the absence of alcohol

A difficulty arose in the analysis of the relaxation data because the latter were obtained at 5 °C whereas the micellar properties of the system were measured at 25°C However, estimates of the micellar properties of the mixed systems at 5°C were obtained by assuming that the known temperature dependence of the mean aggregation number and cmc for TTAB also holds for these mixed systems The values of k_1^-, k_1^+ and $\bar{n}$ for TTAB in H_2O and for TTAB in several aqueous alcoholic mixtures obtained from this analysis are shown in Table 2 The solubilization of alcohol in the micelle is observed to decrease k_1^- and this result is likely due to the concomitant decrease in micelle surface charge density that arises during this process [24] Pentanol has a greater effect than n-butanol because it has a larger partition coefficient The value of k_1^+ is seen to depend little on alcohol concentration This is not too surprising as k_1^+ depends on the diffusion coefficient of the surfactant, and on the electrostatic repulsive potential at the head group region of the micelles The presence of neutral alcohols in this region appears not to effect this potential in a significant way These data show that incorporation of a medium chain length alcohol molecule into a mixed micelle reduces, slightly, the exit rate constant of the surfactant from the mixed micelle but has little effect on the association rate constant of the surfactant

Table 2 Values of exit rate constant of surfactant from TTAB micelles and TTAB–alcohol mixed micelles[a]

Solvent	$\bar{n}$	k_1^- (s^{-1}) $\times 10^{-6}$	k_1^+($M^{-1}s^{-1}$) $\times 10^{-8}$
H_2O	80	2 4	7
H_2O–0 2 M butanol	55	1 2	5
H_2O–0 1 M pentanol	45	0 76	5

[a] From ref 24

5.3 Alcohol and Surfactant Exchange between Mixed Micelles of Short to Medium Chain Length Alcohols and a Short Chain Length Surfactant

More recently, ultrasonic absorption studies at 25 °C have been reported[30 31] for the fast exchange processes for both the alcohol and surfactant components of mixed micelles consisting of decyltrimethylammonium bromide (DTAB) and the alcohols, n-propanol to n-pentanol and BE The use of a short chain-length surfactant causes the fast exchange rate for the surfactant from the mixed micelle to shift to high frequencies It was possible to observe this relaxation by extending the frequency range of sound absorption measurements to *ca* 0 7 MHz using the resonator technique The data show the existence of two relaxation processes which can be attributed to the alcohol and surfactant exchange processes of equation 6 The relaxation times were found to be sufficiently separated so that the analysis of the data according to equation 5 did not give rise to rather inaccurate values Nevertheless, the experimental errors in the estimated values of the two relaxation times are larger than what one would expect for a single relaxation process The difference in the relaxation times was considered sufficiently large that it could be assumed the two exchange processes were not strongly, kinetically coupled This enabled analysis of the relaxation data by means of equations 7 and 8 rather than having to use the complex expressions[21] for the case where the two processes are strongly coupled *i e*, $k_2^- \cong k_1^-$ Figure 2 shows a typical result obtained for α/f^2 *versus* frequency for systems investigated The solid line represents the best fit of the data according to equation 5 for the case of two relaxation processes The analysis of τ_1 for both components to give values of k_1^- and k_2^-, equations 7 and 8, required estimates of the equilibrium properties of the mixed micelles These were obtained from conductance and fluores-

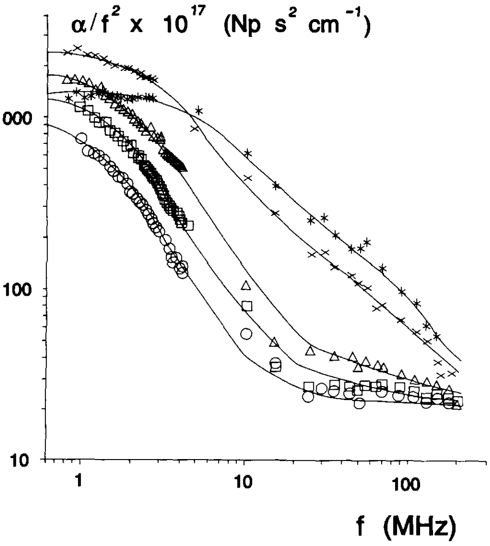

Figure 2 Plot of α/f^2 *versus* frequency at 25 °C for solutions containing 0 12 m DTAB and various concentrations of n-propanol (○) 0 0 m, (□) 0 20 m, (△) 0 49 m, (X) 1 60 m and (*) 2 23 m
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cence quenching measurements. It was shown that equation 7 could be further simplified depending upon the degree of partitioning of the alcohol between the micelle and bulk phase.[30,31] A typical graphical representation of the relaxation frequencies to obtain estimates of k_1^- and k_2^- is shown in Figure 3.

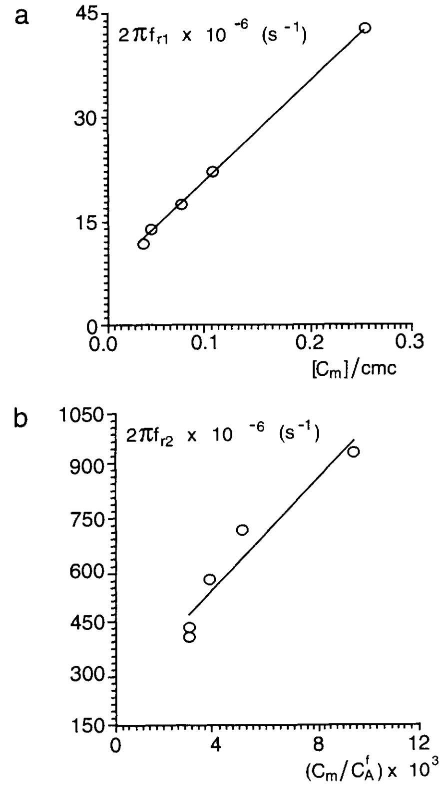

Figure 3 Plot of (a) $1/\tau_{1,S}$ *versus* C_m/cmc and (b) $1/\tau_{1,A}$ *versus* C_m/C_A^f for solutions at 25°C containing 0.12 m DTAB and various concentrations of n-propanol.

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Values of the kinetic parameters for aqueous solutions of DTAB and mixed micelles of DTAB + alcohol derived from the relaxation data using the Aniansson model are presented in Table 3. The data show that the exit rate of the monomer surfactant, k_1^-, decreases with increasing chain length of the n-alcohol solubilized in the mixed micelle. It is also evident that the value of k_1^- for the DTAB–BE system does not fit into the above trend. Rather, k_1^- has a value that is approximately the same as that for a monomer surfactant dissociating from a regular micelle of DTAB. As well, the magnitude of the exit rate of BE from the mixed micelle falls between the values for n-butanol and n-pentanol.

Table 3 Values of rate constants for the fast exchange processes of alcohol and surfactant between DTAB + alcohol mixed micelles and the bulk phase

Alcohol	$k_1^{+,a}$(M^{-1} s^{-1}) × 10^{-9}	k_1^-(s^{-1}) × 10^{-8}	$k_2^{+,b}$(M^{-1} s^{-1}) × 10^{-10}	k_2^-(s^{-1}) × 10^{-10}
none[c]	4.5	3.0		
n-propanol	2.2	1.4 ± 0.1	2.4	4.9 ± 2
n-butanol	1.7	1.1 ± 0.3	5.6	3.5 ± 1
n-pentanol	1.5	0.95 ± 0.3	8.3	1.7 ± 0.4
n-butoxyethanol	5.1	3.1 ± 0.7	2.5	2.2 ± 0.6

[a] Calculated using the cmc in the absence of alcohol where $k_1^+ = k_1^-$/cmc.
[b] Calculated fromthe relationship $K = k_1^+/k_2^-$. [c] Obtained using the data from *J. Phys. Chem.*, 1988, **92**, 2305.

These results can be reconciled as follows. Micellar aggregates exist by virtue of a delicate balance between attractive and repulsive intermolecular forces that are operative in these systems. On the one hand, stabilizing contributions arise from both the solvation of head groups and the hydrophobic interactions that occur between the hydrocarbon chains of the surfactant in the micelle interior. On the other hand, destabilizing repulsive forces result from electrostatic repulsion between the charged head groups of the ionic surfactant monomers when they are in proximity to one another in the micelle. The decrease in the magnitude of k_2^- in mixed micelles containing the n-alcohols, as the hydrocarbon chain length of the n-alcohol increases, is directly related to the increase in hydrophobic interaction between the alkyl chains of the n-alcohol and surfactant. The changes in intermolecular forces in the head group region due to the replacement of water molecules by the hydrophilic moiety of the n-alcohol appear to have no net effect on the exit rates and this may be due to compensatory effects. For example, while the solubilization of alcohol molecules between the ionic surfactant head groups decreases the magnitude of the destabilizing repulsive forces, the weaker ion–dipole stabilizing forces that arise when water dipoles are replaced by alcohol dipoles may also be diminished in a nearly offsetting manner.

The results for k_1^- and k_2^- in DTAB–BE mixed systems require a more detailed explanation. The magnitude of k_2^- for BE lies between the values for n-butanol and n-pentanol, which suggests that the n-butyl segment of BE is embedded in the mixed micelle interior. However, the magnitude of k_1^- in the presence of BE is relatively greater than expected when a comparison is made with the values obtained for the n-alcohol series. In fact, k_1^- in the presence of BE is approximately the same as k_1^- in the absence of alcohol. Thus, there appears to be weaker ion–dipole stabilizing forces when water dipoles are replaced by BE dipoles in the head group region of the DTAB micelles.

There are two independent observations that support this speculation. It has been shown[32] that the surface charge density of DTAB–BE mixed micelles is generally greater than that of DTAB–n-alcohol systems. Consequently, the repulsive forces in the head group region are expected to be greater than in the case of the n-alcohols. It has also been reported[33] that the Gibbs energy of transfer of a homologous series of alcohols, having the general formula $C_4(EO)_xOH$, where $0 \leq x \leq 4$, from the bulk to the cationic micellar phase is independent of the number of EO segments in the alcohol. If the EO segment of BE locates on the surface of the micelle, as the previous results may suggest, then the relatively stronger ion–water dipole interactions are replaced by weaker ion–EO dipole interactions. Of the many sterically possible conformers of the EO segment, a very large majority have small or no dipole moment. If these latter conformers are favoured when BE is solubilized in the mixed micelle, then a reduction in the stabilizing forces in the head group region of DTAB–BE relative to that in DTAB–n-alcohol mixed micelles can explain, qualitatively, the observed differences in the dissociation rate constants of components in these systems. It would appear from these results that the dissociation rate constant of an alcohol from the mixed micelles is mainly controlled by the hydrophobic interactions whereas the exit rate constant of the ionic surfactant is affected by changes in the forces of electrostatic interaction within the head group region and the surrounding solvation sheath.

It can be shown[31] that the decrease in the exit rate of the surfactant represents a measure of the Gibbs energy of stabilization per CH_2 group of the alcohol. From $\Delta G_S = RT\mathrm{d}\ln(k_1^-)/\mathrm{d}n_c$, a plot of ln k_1^- *versus* n_c (number of carbon atoms in the n-alcohol) is linear and gives a value of $\Delta G_s = -450$ J mol^{-1} per CH_2 for the DTAB–n-alcohol systems.

Analysis of the experimental sound absorption data[30,31] according to the phenomenological model proposed by Hall[20] gave slightly larger values than those obtained from use of the Aniansson model, however, the qualitative picture remained unchanged

6 Kinetics of Slow Micelle Formation–Breakdown in Mixed Alcohol and Ionic Surfactant Systems

The temperature-jump method using optical detection has been used to study the slow relaxation time, τ_2, characterizing the process of micelle formation–breakdown The effect of alcohols on this process in mixed micellar systems has been the focus of extensive studies [24 34] Specifically, the behaviour of τ_2 for systems containing the surfactants tetradecyl- and hexadecylpyridinium bromide (TDPB and HDPB) and chloride (TDPC and HDPC), and hexadecyltrimethylammonium chloride (CTAC) with the series of alcohols, ethanol to n-decanol, as well as benzyl alcohol, was studied for addition of alcohols to moderately concentrated surfactant solutions The changes in τ_2 were found to be very sensitive to the nature, chain length, and concentration of the added alcohol, as illustrated in Figures 4 and 5 The addition of medium chain length alcohols (up to n-pentanol) to 0 3 M solutions of surfactant induces an increase of τ_1^{-1} by up to a factor of 10^4, *e g* , n-pentanol added to HDPC, (Figure 4) Longer chain alcohols show τ_2^{-1} going through a maximum at an alcohol concentration that decreases as the alcohol chain length increases Nevertheless, at low alcohol concentration the effect of the alcohol is to increase τ_2^{-1} (Figure 5) Since the average lifetime of a micelle increases with τ_2, the mixed micelles containing short-chain alcohols and surfactant are observed to breakdown much more quickly than the regular micelles Also, the decrease in τ_2^{-1} that occurs with long-chain alcohols at higher concentration is analogous to the observed effect on τ_2 when linear alkanes are solubilized in surfactant systems Alkanes are known to be solubilized in the interior of micelles and the micelles tend to become less anisotropic and less polydisperse according to fluorescence-probing and quasi-elastic light-scattering studies [34]

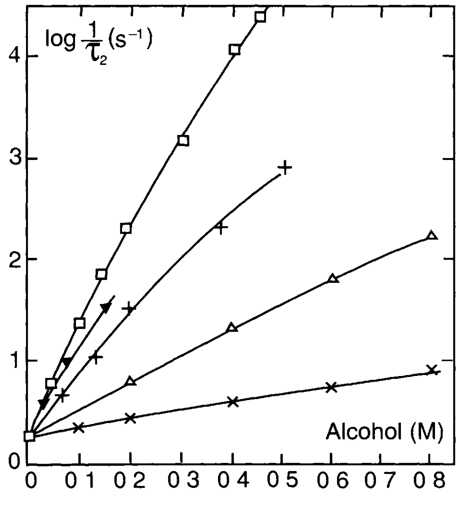

Figure 4 Effect of the concentration of added alcohol on $1/\tau_2$ for a 0 3 M HDPC solution, (X) ethanol, (△) 1-propanol, (+) 1-butanol, (▼) benzyl alcohol, (☐) 1-pentanol $T_f = 25\,°C$
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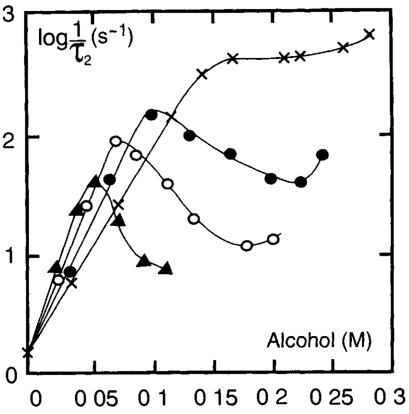

Figure 5 Effect of the concentration of added alcohol on $1/\tau_2$ for 0 3 M HDPC solution (X) 1-hexanol, (●) 1-heptanol, (○) 1-octanol, (▲) 1-decanol $T_f = 25\,°C$
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The following qualitative explanation of the τ_2^{-1} behaviour as a function of alcohol concentration can be made The short-chain alcohols appear to solubilize in the palisade layer of the micelle, the outer shell region which contains the head groups and approximately one to two carbon atoms of the alkyl chain next to the head groups However, while the long-chain alcohols at low concentration solubilize in the palisade layer with the OH group anchored at the micelle surface between the surfactant head groups, at higher concentrations when the palisade layer is saturated, they solubilize in the micelle interior

A more detailed explanation of the effect of alcohols on τ_2^{-1} has been presented[34] based on the following arguments Because of the experimental concentrations used for the surfactants, the micelle breakdown–formation by means of reactions shown in equation 11 cannot be neglected The complex expressions derived[19] for the terms in equation 12 were used to try to determine what parameter changes are most important in explaining the dependence of τ_2^{-1} on alcohol concentration It was concluded that the average dissociation rate constant for τ_2^{-1}, the average being taken over all micelles of different aggregation numbers and assuming there was no potential energy barrier to equation 11, rapidly increases upon addition of alcohol A large part of this rapid change is due to increased micelle polydispersity as shown by quasi-elastic light-scattering results [34] The explanation given[34] for the change of the concentration of submicellar aggregates (second region in the aggregate size distribution curve discussed in Section 4 1 2) is linked to the change in the nature of these aggregates as alcohol is added In the absence of alcohol the submicellar aggregates of ionic surfactant should possess some charge close to their aggregation number However, when alcohol is added, the aggregates in this region may be comprised mainly of alcohol molecules with fewer surfactant ions Thus the aggregates have lower electrical charge and their concentrations will be larger due to diminished repulsive interactions This should increase the contribution to τ_2 of both reactions 10 and 11

Consequently, at low alcohol concentrations, as long as the alcohol is solubilized in the palisade layer, all alcohols behave similarly Under these circumstances, large surfactant-rich aggregates and small alcohol-rich submicellar aggregates are in dynamic equilibrium At higher alcohol concentrations, the alcohol begins to dissolve in the micelle interior Micellar shape becomes anisotropic and the small subaggregates make up the interface between the alcohol solubilized in the micelle interior and the bulk phase This results in a decrease in polydispersity and, hence, in τ_2^{-1} Finally, the alcohol concentrations at which large proper micelles and small alcohol-rich aggregates can coexist decreases as the alcohol chain length increases

7 Conclusion

The material discussed in this article has been limited to a rather narrow, but nevertheless important, area of dynamic processes in mixed micellar aggregates Some background and theory about several of the techniques used to obtain experimental data and the theoretical models developed to analyse macroscopic properties of the aggregates in terms of molecular events were included No attempt was made to discuss thermodynamic properties that can be derived from an analysis of the amplitude of relaxation processes As predicted by theory, the solutions of surfactant in the presence of alcohol are characterized by three relaxation processes

The incorporation of alcohol and surfactant species into a mixed micelle are mainly diffusion controlled The addition of alcohol reduces the rate constant for the fast dissociation of both surfactant and alcohol from a mixed micelle As well, added alcohol creates extreme lability of the slower formation–breakdown process of the micellar aggregates Within the accuracy of current measurements, and for the few systems that have been studied, there does not appear to be a strong dependence of these dynamic processes on the chemical nature of the surfactant head group and counterion The trends in the observed behaviour of the rate constants of the fast exchange process in mixed micelles can be rationalized in terms of the intermolecular forces arising from solvation of the head groups, electrostatic repulsions between the head groups, and hydrophobic interactions between alkyl chains of the components

The complexity of the relationships linking rate constants to relaxation times for these systems and the requirement of extensive complementary information about the equilibrium properties of the mixed micelles has limited the choice of systems investigated Even under these circumstances it is necessary to make some assumptions to characterize the relaxation processes in terms of molecular events Notwithstanding these difficulties, such studies have and are continuing to make an important contribution to the understanding of the dynamics of mixed micellar systems It is anticipated that they will serve as a useful benchmark in the study of more complex surfactant-containing systems such as microemulsions and vesicles, when the results are studied in conjunction with other techniques

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