Kinetic and Equilibrium Studies on the Exchange Process of n-Hexanol and Cetyl Trimethyl Ammonium Bromide (CTAB) Micelles

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ABSTRAK

Kajian kinetik menggunakan kaedah pengenduran ultrasonik dalam larutan misel campuran bagi n-heksanol dan setil trimetil ammonium bromida telah menunjukkan pengenduran tunggal yang nyata. Ini adalah berkaitan dengan proses pertukaran melibatkan alkohol dan misel campuran. Pengukuran keseimbangan yang menentukan kepekatan monomer heksanol telah dilakukan dengan menggunakan kaedah gas kromatografi. Gabungan data dari pengukuran pengenduran dan keseimbangan telah dianalisa menggunakan kaedah fenomenologikal di mana parameter-parameter kinetik dan termodinamik boleh didapati untuk proses pertukaran berkenaan. Kesimpulan utama dari kajian ini ialah proses penyatuan monomer heksanol kepada misel campuran adalah hampir sama dengan proses peresapan terkawal.

ABSTRACT

Kinetic studies using ultrasonic relaxation method in the mixed micellar solutions of n-hexanol dan cetyl trimethyl ammonium bromide have shown a well-defined single relaxation. This is associated with the exchange process involving the partitioning of alcohol with the mixed micelle. The equilibrium measurement which monitors the monomer concentration of n-hexanol was measured using head space analysis involving gas chromatography. The combined relaxation and equilibrium data were analysed using a phenomenological treatment in which the kinetics and thermodynamics parameters were evaluated for the exchange process. The main conclusion from this work is that the association of n-hexanol to the the mixed micelles is almost a diffusion controlled process.

Keywords: mixed micelles, exchange process

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INTRODUCTION

Microemulsions are thermodynamically stable isotropic fluid phases containing substantial amounts of surfactant, co-surfactant (usually alcohol), oil and water with many industrial and pharmaceutical applications (Robb 1982; Mittal 1982). The key ingredient which is thought to control the properties of microemulsions is the the mixture of surfactant and alcohol co-surfactant. As a result, much attention has been focused on the properties of surfactant-alcohol mixtures.

In dilute micellar solutions, alcohols such as butanol, pentanol and hexanol usually form mixed micelles with the surfactant; the alcohol is thought to reside in the palisade layer of the micelles. Incorporation of alcohol into the micelles results in changes of micellar properties of the surfactant system. Zana *et al.* (1981) found that addition of alcohol of medium chain length decreases the CMC of several alkyl trimethylammonium bromide surfactants followed by a strong increase in the degree of counterion dissociation (α) at higher concentrations of added alcohol. It was found that the molecular weight of the micelles and hence their aggregation number decreases when the alcohol concentration is increased. These observations imply that these effects are due to partial solubilization of alcohol by the surfactant micelles. The alcohol is solubilized in the palisade layer of the micelle with the alcohol molecules intercalated between the surfactant ions, and hence increases the average distance between the ionic head group of the surfactant. This results in a decrease in micelle surface charge density and in turn an increase in ionization. This behaviour was supported by Bostrom *et al.* (1989). The increasing distance between the surfactant head group due to the alcohol molecules also results in a weakening of the electrostatic repulsion. This promotes the association of the surfactant with the alcohol molecules at a lower concentration, and hence reflects the decrease of CMC. The decrease in aggregation number of surfactant micelles due to solubilization of alcohols has been claimed by several authors (Birdi *et al.* 1978; Zana *et al.* 1981) as a result of destabilization of micelles. Dissociation of some surfactant molecules occurs at the expense of replacement by the alcohol molecules.

Solubilization of alcohol by the surfactant micelles causes abrupt changes in the microscopic properties of the system (Bucklund *et al.* 1986; Vikholm *et al.* 1987). This has been interpreted as a change in the alcohol solubilization pattern in which two solubilization sites for the alcohol are involved, i.e. the palisade layer and the interior of the micelle; in the latter case swollen micelles are formed. On the other hand, Stilbs (1982) found that solubilized short chain alcohols cause a breakdown of surfactant micelles above a certain total surfactant-alcohol concentration ratio which is in contrast with the formation of swollen micelles. The interpretation of

the solubilization behaviour of alcohol by the surfactant micelles as reported above has been the subject of some controversy and therefore it seems desirable to carry out more systematic and independent studies on these systems. In the present work, our strategy was to combined equilibrium data from the head space analysis (which involved gas chromatography with ultrasonic relaxation experiments) so that new thermodynamic and kinetics parameters for the partitioning process could be evaluated.

MATERIALS AND METHODS

Cetyl trimethylammonium bromide (CTAB) and n-hexanol were obtained from BDH and used directly as received. The hexanol-CTAB solution mixtures were prepared in a series of hexanol concentrations at two constant concentrations of CTAB, i.e. 0.05 and 0.075 mol dm^{-3}.

The kinetic measurements on the solution mixture were made using the Eggers ultrasonic resonance technique which has a frequency range of 0.4 to 17 MHz. All measurements were made at the constant temperature of 25°C.

Equilibrium measurements concerning the partition of hexanol between the aqueous and micellar CTAB micelles were carried out using head space analysis involving a Shimadzu model G.G.8A gas chromatography fitted with a CRIB integrator and flame ionization detector. The procedure used has been described elsewhere (Smith *et al.* 1989). The partitioning data were also measured at two concentrations of CTAB at varying concentrations of hexanol up to 0.18 mol dm^{-3}. All measurements were taken at 25°C.

RESULTS AND DISCUSSION

The results from equilibrium measurements are displayed in *Fig. 1*; the amount of solubilized hexanol in the mixed micelle $\left(C_2^m\right)$ is plotted as a function of hexanol monomer concentration (m_2). The total hexanol concentration $C_2 = C_2^m + m_2$. In both cases C_2^m is a linear function of m_2. For purposes of the present work the partition coefficient, K, for hexanol in the two phases is defined as follows:

$$K = \frac{C_2^m}{m_2 C_1} \tag{1}$$

where C_1 represents the CTAB concentration. Using this equation, the value of *K* can be obtained from the slope of the plot in *Fig. 1* as follows:

K(0.05 mol dm^{-3} CTAB) = 43.0 mol dm^{-3}
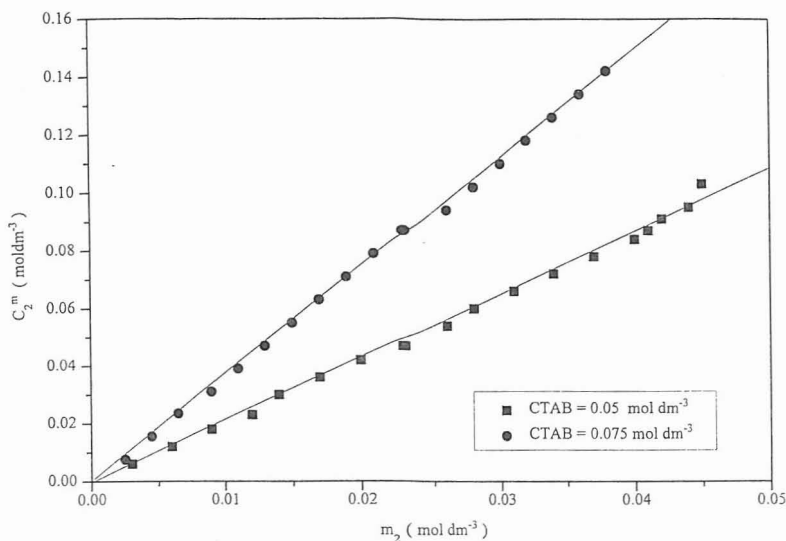K(0.075 mol dm^{-3} CTAB) = 50.0 mol dm^{-3}

Fig. 1. Plot of amount of solubilized hexanol $\left(C_2^m\right)$ as a function of aqueous hexanol (m_2)

In the ultrasonic measurements, typical relaxation curves showing the plot of α/f^2 against f are given in *Fig. 2* and *3* for both CTAB concentrations where α is the sound absorption coefficient and f is the frequency. These results can be fitted within experimental accuracy using the following equation:

$$\frac{\alpha}{f^2} = \frac{A}{1+\left(f/f_0\right)^2} + B \tag{2}$$

where A is the relaxation amplitude, B is the background absorption which is independent of frequency and f_0 is the relaxation frequency. In all cases, the experimental data were described by a single relaxation spectrum in the experimental frequency range. This was associated with the exchange process of hexanol between the aqueous and micellar phases since the exchange process involving the CTAB monomer and the mixed micelles is too slow and "frozen" out within the experimental range as reported by Hall *et al.* (1977), Gettings *at al.* (1978) and Gormally *et al.* (1985). Furthermore, pure alcohol solutions up to the solubility limit did not show any relaxation; a relaxation was only observed when the alcohol was added to micellar surfactant solution. The dynamic equilibrium existing in solution can be represented as follows. In this case only step 1 in Scheme 1 is observed.
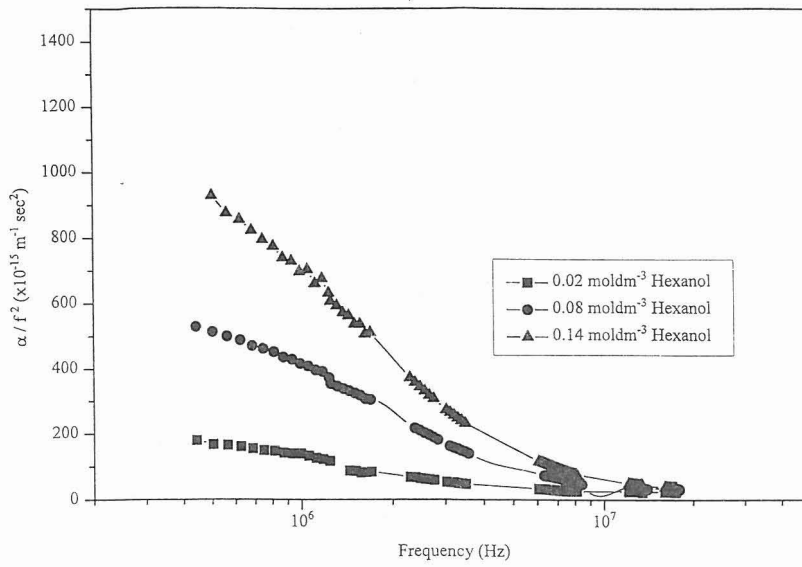
Fig. 2. Plot of α/f^2 versus frequency for 0.05 mol dm^{-3} CTAB
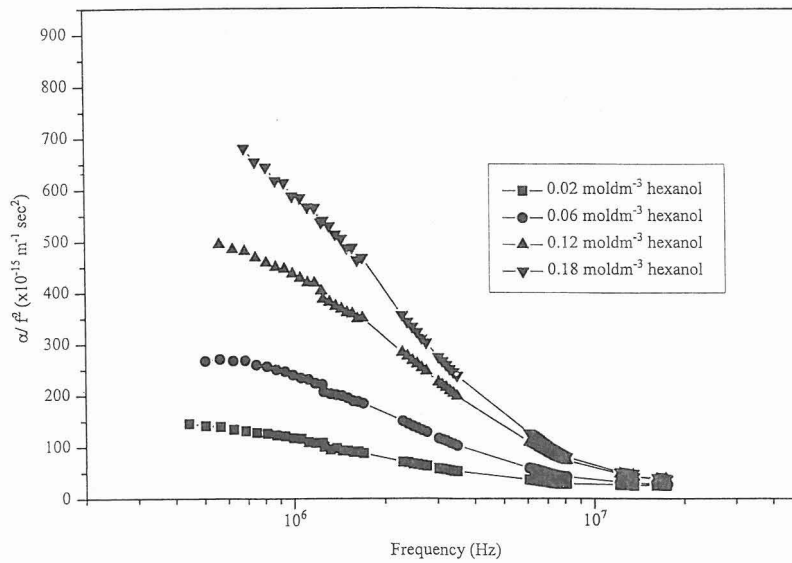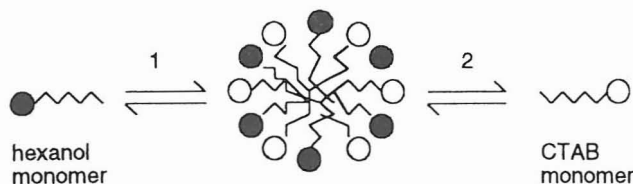with added n-hexanol

Fig. 3. Plot of α/f^2 versus frequency for 0.075 mol dm^{-3}
CTAB with added n-hexanol

hexanol
monomer

CTAB
monomer

Scheme 1

The pertinent relaxation parameter required for the phenomenological treatment are $\tau_1 = 1/2\pi f_c$, which is the relaxation time, and $\mu_{max} = 1/2\ Acf$, which is the maximum absorption per wavelength; c is the velocity of sound through the sample. The relaxation data associated with step 1 in the scheme above were analysed using the phenomenological approach because it has been successfully used in determining the thermodynamic and kinetic parameters of a number of alcohol-surfactant mixtures (Gettings *at al.* 1978; Gormally *at al.* 1985; Smith *et al.* 1989; Kelly *et al.* 1989). For the relaxation process in question, which essentially occurs at constant micelle concentration, C_m, and constant micellar concentration, C_1, the maximum absorption per wavelength (μ_{max}) has been shown by Gormally *et al.* (1985) to have the following concentration dependence:

$$\mu_{max} = \left[\frac{\pi(\Delta V)^2}{2RT_{K_s}}\right]\frac{m_2 C_2^m}{C_2} \qquad (3)$$

where ΔV is the reaction volume change, K_s the adiabatic compressibility, C_2 the total hexanol concentration; R and T have their usual meaning. According to Eq. 3, a plot of μ_{max} against $(m_2 C_2^m)/C_2$ should be a straight line passing through the origin with the slope equal to the thermodynamic term in brackets from which ΔV can be evaluated. For the two CTAB concentrations, these plots (shown in *Fig. 4*) display the linearity predicted by Eq. 3 above. The following ΔV values have been obtained from the plots:

0.05 mol dm^{-3} CTAB; $\Delta V = 5.6$ cm^3 mol^{-1}

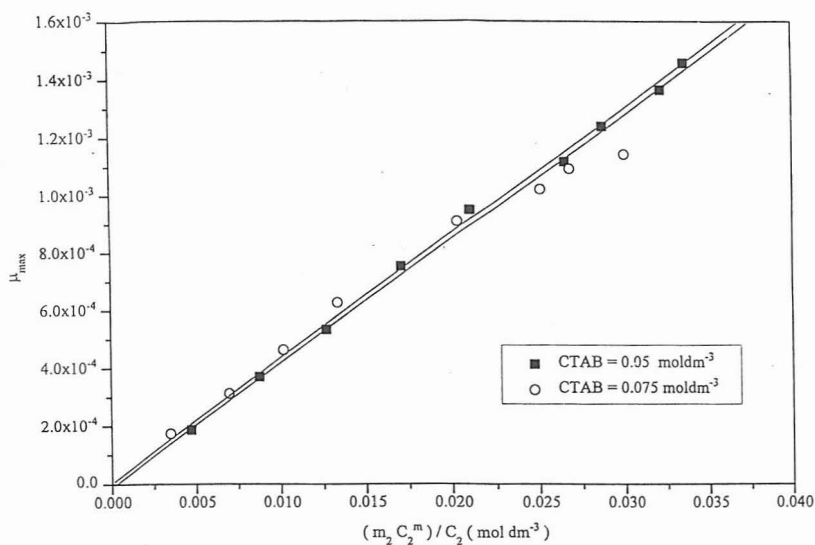0.075 mol dm^{-3} CTAB; $\Delta V = 5.4$ cm^3 mol^{-1}

Fig. 4. Maximum absorption per wavelength (α_{max}) as a function of $((m_2\, C_2^m)/C_2$.

The kinetic parameters of the partitioning behaviour of alcohol can be investigated using the phenomenological equation

$$\frac{\mu_{max}}{\tau l} = \left[\frac{\pi(\Delta V)^2}{2RT_{K_s}}\right] R \qquad (4)$$

where R represents either the forward rate or backward rate of the equilibrium (step 1) being perturbed by the sound wave, i.e. alcohol associating to or dissociating from the mixed micelle. In dilute hexanol-CTAB solutions it is expected that the solubilized hexanol resides in the palisade layer of the micelle. In these cirumstances the kinetics of the dissociation of hexanol molecule from the mixed micelle is expected to be a first-order process whose rate is directly proportional to the amount of solubilized hexanol.
Thus,

$$R_b = k^- C_2^m \qquad (5)$$

where k is the backward rate constant. Combination of Eqs. 4 and 5 rearrangement gives

$$\frac{\mu_{max}}{\tau_1} = \left[\frac{2RT_{K_s}}{\pi(\Delta V)^2}\right] = k^- C_2^m \qquad (6)$$

In Eq. 6. U_{max} and τ_1 are known from the relaxation experiments, and the thermodynamic terms on the left-hand side are the inverse of the slope of plots in *Fig. 4* while C_2^m follows from the head space data. Thus for a first order dissociation, a plot of the left-hand side of Eq. 6 against C_2^m should be a straight line passing through the origin. The plots for the two concentrations of CTAB studies in this work are shown in *Fig. 5*. In the dilute hexanol region, the term on the left-hand side is directly proportional to C_2^m giving good straight lines passing through the origin. In this region it is clear that the backward rate is a first-order process whose rate is directly proportional to the amount of solubilized hexanol. However, above a certain hexanol concentration the reaction rate appears to level off to a constant value. The levelling-off of the reaction rate takes place only in the concentrated alcohol solutions.
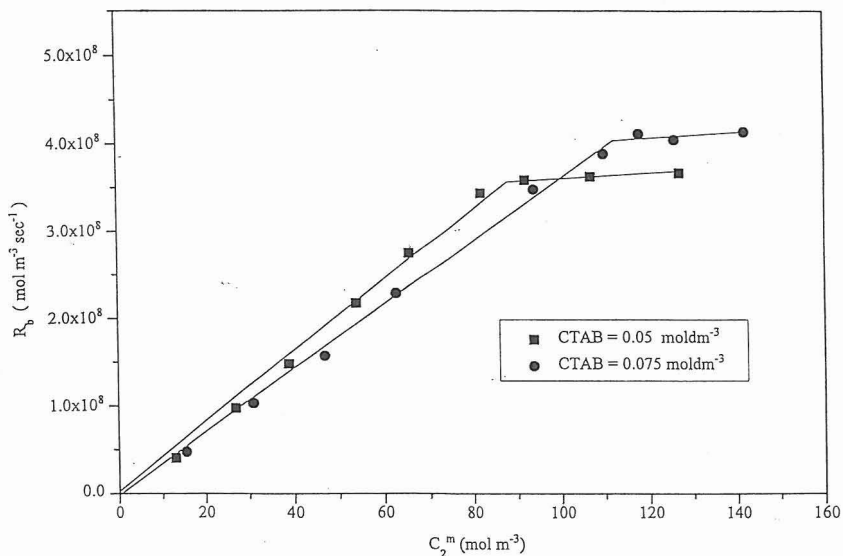

Fig. 5. Backward rate (R_b) as a function of solubilized n-hexanol concentration $\left(C_2^m\right)$

We turn our attention to discuss the experimental data described above in relation to the solubility behaviour of hexanol in CTAB micelles with special attention to changes in the solubility pattern.

a)   The partition coefficient, K as defined by Eq. 1 is constant over the hexanol concentration range 0.02-0.18 dm^{-3} as is demonstrated by the linearity of the plots in *Fig. 1*.

b)   The maximum absorption per wavelength, μ_{max} measured from the ultrasonic experiment monitors the thermodynamic parameter, ΔV, which is the volume change between the "free" and "solubilized" hexanol. The linearity of plots shown in *Fig. 4* for both 0.05 and 0.075 mol dm^{-3} of CTAB solution shows that ΔV is constant at all hexanol concentrations with a value of 5.5 ± 0.1 cm^3 mol^{-1}.

c)   A more specific indicator for kinetic behaviour, μ_{max}/τ_1 which according to the phenomenological approach monitors the backward rate associated with the partitioning process, shows deviation from linearity at the higher hexanol concentrations.

Therefore, on balance, the two equilibrium measurements which monitor different aspects of the partitioning described in (a) and (b) above do not show any evidence of a change in solubilization pattern. On the other hand, the kinetic information indicates clear deviation at high hexanol concentrations as shown in *Fig. 5*. The constant R_b at this high concentration of hexanol may be associated with the solubilization behaviour of the alcohol. A previous report by Vikholm *et al.* (1987), who also observed a break in their experimental data using other techniques at this high concentration, claimed that the breakpoint was associated with the solubilization of alcohol in the core of the CTAB micelles. If this is true and on assumption that the hexanol in the interior does not take part in the exchange process, then Rb will depend only on the concentration of hexanol in the palisade layer. If we assume that the palisade layer is "saturated" and has a constant concentration after the breakpoint, then it is expected from Eq. 5 that Rb will also be constant. However, this is only a crude assumption since the solubilization of alcohol into the interior of the micelle is still a matter of controversy and the assumption that alcohol in the micellar core does not take part in the exchange process is questionable. With the lack of any obvious deviation in the equilibrium experiments we conclude that the evidence from the ultrasonic measurements is not convincing enough to lend support to a change in solubilization of hexanol. The observation in (c) above which is thought to be associated with a change in solubilization behaviour is debatable since a similar behaviour is also observed in a pure surfactant system involving monomer-micelle exchange process at high surfactant concentrations. Furthermore, the ultrasonic measurements are made close to the phase boundary where possible additional contribution (e.g. from concentration fluctuation or phase changes) to the relaxation data may occur. In

addition, the solution mixtures at high hexanol concentrations appeared to turn cloudy with time, suggesting that their thermodynamic stability is questionable.

The phenomenological treatment as illustrated in *Fig. 4* and *5* allows us to determine the forward rate constant (k^+) from the relaxation data. As mentioned previously, in dilute hexanol solutions, the backward rate describing the dissociation of hexanol from the mixed micelle is directly proportional to the solubilized hexanol, confirming that it is a first-order rate process. On similar grounds one expects the forward rate, R_f, describing the association of hexanol to the mixed micelle to be a bimolecular process proportional to the product of the concentrations of free hexanol, m_2, and the mixed micelle. Thus,

$$R_f = k^+ m_2 \text{ [mixed micelle]} \tag{7}$$

where k^+ is the forward rate constant, at equilibrium $R_f = R_b$, so that from Eq. 5 and 7 we obtain

$$k^+ m_2 [mixed\ micelle] = k^- C_2^m \tag{8}$$

or

$$[mixed\ micelle] = \frac{k^- C_2^m}{k^+ m_2}$$

If we consider the limit of this equation as $C_2^m \to 0$, then

$$[mixed\ micelle] = \frac{C_1}{n} \tag{9}$$

where n is the aggregation number of CTAB micelles. From Eq. 1, $K = \dfrac{C_2^m}{m_2 C_1}$ and upon rearranging Eq. 8 and 9 the aggregation number (n) takes the following form

$$k^+ = k^- K n \tag{10}$$

The backward rate constant (k) can be evaluated from the linear part of *Fig. 5*. For 0.05 mol dm^{-3} CTAB the value is 4.39×10^6 s^{-1} with $K = 43.0$ mol dm^{-3}. The aggregation number of CTAB is about 80 (Smith *et al.* 1989). Under these circumstances, the forward rate constant (k^+) for the

association of n-hexanol with CTAB micelles can be calculated, and has the value of

$$k^+ = 1.51 \times 10^{10} \text{ mol dm}^{-3} \text{ s}^{-1}$$

This value is close to the diffusion control value of $k_d = 1.74 \times 10^{10}$ mol dm^{-3} s^{-1} which is calculated from Eq. 11

$$k_d = 4\pi\left(D_a + D_m\right)R_c N \times 10^{-3} \qquad (11)$$

Here N is the Avogadro number, D_a and D_m are the respective diffusion coefficient of n-hexanol and the mixed micelle, R_c is the effective reaction distance and factor 10^{-3} arises because the concentrations are expressed in mol dm^{-3}. In the present circumstances, R_c is effectively equal to the micellar radius and $(D_a + D_m) \approx D_a = 9 \times 10^{-6}$ cm^{2}s^{-1} according to Glasstone (1941).

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