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VISCOSITY STUDIES ON CTAB-*p*-NITROPHENYL ACETATE SYSTEMS*

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The viscosities of cetyltrimethyl ammonium bromide (CTAB) solutions with and wihout *p*-nitrophenyl acetate (PNPA) have been measured with suspended level viscometers at 30° in distilled water, in carbonate–bicarbonate buffer at pH 9.2 and in various solutions of KBr. The reduced specific viscosity of the micelles of each system was calculated and plotted against micellar concentration. Changes in the physical nature of the micelles, i.e. size and particularly shape in the region of $10^{-2}M$ CTAB have been proposed and discussed.

INTRODUCTION

During the last few years there have been an increasing number of investigations into the modifying effect of surfactants on the rates of organic reactions, both with regard to their influence on drug stability and as models for enzymatic and other biological reaction. A number of comprehensive reviews have been published which are largely qualitative, although some attempts have been made to elucidate the mechanism of the surfactant effects which are still not fully understood [1–5].

There are several reports in the literature on the effect of cationic surfactants on the hydrolysis of PNPA. Meakin *et al.* [6] in their surfactant–ester study showed that the 'surfactant-effect ratio' (SER) defined as the ratio of the rate constant in presence of CTAB to that in absence of CTAB [7], increases in the presence of PNPA with increase in CTAB concentration up to a maximum value of 4.2 at a surfactant concentration of $9.6 \times 10^{-3}M$. Examination of the literature shows that the maxima reported by a number of workers for CTAB-catalysed processes also occur at a concentration in the region of $10^{-2}M$ [8–10] and thus would be taken as a characteristic feature of CTAB accelerated processes. Shetewi [26] has also described kinetic discontinuities at this CTAB concentration in the *surfactant-inhibited* hydrolysis of phenyl acetate.

Cordes and his coworkers [8, 11, 12] have suggested that the fall in rate after the maximum is reached, is due to an increase in counterion (bromide) concentration causing displacement of hydroxyl ions from the area immediately surrounding the micelle surface. However, the maximum in the surfactant curve is not so easily explained by hydroxyl ion displacement when the added salt concentration is kept constant as in buffered systems. Under such circumstances, although the overall ionic strength of the system will increase with the surfactant concentration, provided the size and shape of the micelles remain constant, then the number of counterions per micelle will also remain constant and it is difficult to see how competitive displacement of hydroxide ions from the micellar surface is possible, unless the double layers overlap.

In the present paper we have suggested the possibility of changes in micellar structure causing a change in size and/or shape of the micelles in the region around $10^{-2}M$ CTAB which results in the subsequent fall in the 'SER'. Support for structural changes in micellar size and particularly shape can be provided through viscosity studies. With this aim in view the present work was initiated since measurements of viscosity supplemented wih information from other hydrodynamic studies have provided valuable information about micellar shape, particle size and degree of hydration of surfactant molecules [13, 14]. Comprehensive reviews have been written by Sherman [15], Frisch and Shima [16], Conway and Dobry–Duclauz [17]. Brush [18] has given a vast list of references covering a number of aspects of viscosity.

MATERIALS AND METHODS

p-Nitrophenyl Acetate (PNPA). PNPA (A.R. grade was supplied by Koch–Light Laboratories. The product was

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twice recrystallised from 50% ethanol [19], m.p. 77.5° (lit. 77.5–78°, Bender and Nakamura [20]).

Surfactant. Cetyltrimethyl ammonium bromide (CTAB) of reagent grade (BDH) was purified according to the method described by Mukerjee and Mysels [21], Duynstee and Grunwald [22], m.p. 231.5° (lit. 230–4°)[23].

Buffer Solutions. Delory and King's carbonate–bicarbonate buffer; pH 9.20 (Documenta Geigy, 1962).

Potassium Bromide. A.R. grade, Fisons Scientific Apparatus.

Water. Freshly distilled water from an all-glass still was used.

Measurement of Viscosity. CTAB solutions of various concentrations were prepared in water and in buffer (pH 9.20) and then filtered through a 0.22-m millipore memberane, previously boiled in several changes of double distilled water and dried to remove any wetting agents. Viscosities were then measured at 30° in a suspended-level viscometer, shortened form size 1 viscometer, according to British Standard 188 1957 [24]. The temperature was maintained by using a double-walled LTE viscometric bath; the temperature fluctuations which were recorded at 30 ± 0.05°. For flow times greater than 800 sec, kinetic energy corrections can be ignored and the viscosity calculated from equation (1)

$$\eta = Ctd\,(1) \qquad (1)$$

Where η = viscosity of the fluid, C= constant for a particular viscometer, t = time in seconds and d = density of solution.

The viscometers were cleaned before use with chromic acid and followed by thorough washing with tap water and then running distilled water for 30 min. The viscometers were then dried according to BS 188: 1957 [24].

Relative viscosities were calculated directly from the flow time, ignoring the densities of the solutions as there was no significant change in relative viscosities when density factors were used.

Reduced specific viscosities were calculated from equation (2) (the detailed mathematical derivations are given elsewhere [25]).

$$\frac{\eta_{rel} - 1}{\Delta C} \qquad (2)$$

where η_{rel} is the relative viscosity and ΔC is the concentration of micelles, i.e. (C-CMC) in g/ml.

CMC Measurements. Critical micelle concentrations were determined under the various conditions used in the present investigation by surface tension, light scattering and bromide ion activity methods. Results are shown in Table 2. Full details of the experimental methods and techniques are available [25, 34, 35].

RESULTS AND DISCUSSION

A detailed kinetic investigation on CTAB–PNPA system was undertaken during previous work in this school. The persistent break in the kinetic profiles at CTAB concentrations 8.5 to 9.6x $10^{-3}M$ occur irrespective of pH, buffer concentration and added bromide up to 0.1M [25]. The qualitative picture proposed by Cordes *et al.* [8, 30] based on competitive inhibition and concentration of counterion does not explain satisfactorily the maximum in the critical concentration region of 8.5–9.6x $10^{-3}M$ CTAB since the model does not take account of micelle size or the total number of the micelles present. In the absence of added electorlyte, at constant aggregation number, the number of counterions per micelle will be constant. Both the light scattering studies [31] and the measurement of free counterion concentration by the use of the bromide ion selectrode [25] would suggest that in the PNPA–CTAB system no changes on the level of counterion binding or micellar size take place at least up to $10^{-2}M$. In the presence of a buffer, therefore, as the concentration of CTAB rises the number of counterions per micelle actually falls.

It thus appears that perhaps the micellar structure is different above and below the critical region of CTAB causing a change in size and/or shape of the micelles. If this is so then such changes should be detectable through light scattering and viscosity studies. Such changes have been reported before, through these techniques by Ekwall *et al.* [14] for solution in water and Shetewi *et al.* [32] for phenyl acetate–CTAB solutions in buffer and KCl.

In order, therefore, to examine the changes in physical characteristics of the micelles, i.e. size and particularly shape which are expected to take place around the region of 8.5–9.6x $10^{-3}M$ CTAB and also to give support to our previous light scattering studies [31] viscosity measurements were carried out on various CTAB systems: (i) CTAB with and without PNPA in water alone. (ii) CTAB with and without PNPA in water, i.e. in the absence of buffer but in presence of 10^{-4}, 10^{-3} and 0.1M KBr. (iii) CTAB with and without PNPA in the presence of single strength carbonate–bicarbonate buffer and 10^{-4}, 10^{-3} and 0.1M KBr at pH 9.20.

The concentration of PNPA was kept constant throughout this work at 4.0x $10^{-5}M$. (A previous study showed that over a six-fold concentration range, from 8x 10^{-5} to 5x $10^{-4}M$, the ester concentration has no significant effect on the rate of hydrolysis at pH 9.20 and 30° in the presence

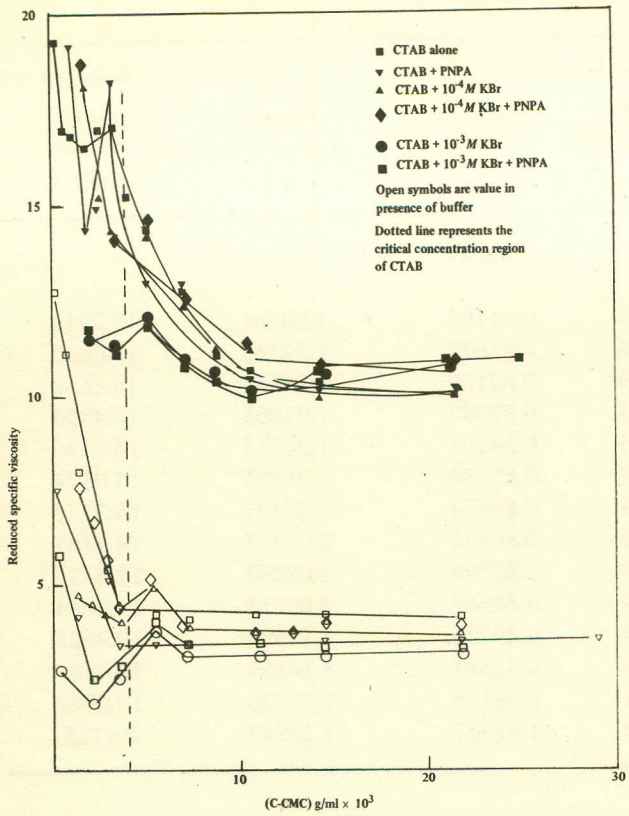

Fig. 1. Reduced specific viscosity against micellar weight under various set of conditions.

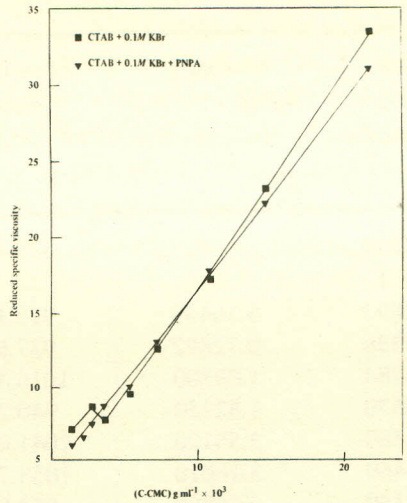

Fig. 2. Reduced specific viscosity against micellar weight for the system in water in presence of 0.1*M* potassium bromide

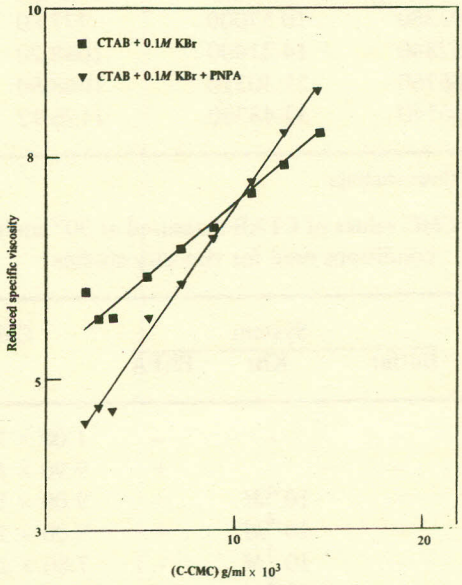

Fig. 3. Reduced specific viscosity against micellar weight for the buffer system in presence of 0.1*M* potassium bromide

of various concentrations of CTAB [25]) Table 1 shows a typical set of viscosity results obtained for CTAB in water alone. The viscosity data plotted as reduced specific viscosity (in terms of micellar concentration) against micellar concentration are given in Figs.1–3. CMC values used to obtain micellar concentration are presented in Table 2.

The reduced specific viscosity plot for CTAB in water alone is very similar to that reported by Shetewi [26]. It is clear that although the viscosity of the systems rises with increased CTAB concentration, *the reduced specific viscosity* (η_{red}) decreases. This suggests that either larger or more assymmetric particles exist at the lower CTAB concentrations.

The relatively high values of η_{red} obtained for CTAB in water alone as compared to other systems, could be due to the electroviscous effect [27] which will be absent at high ionic strengths. The lower the ionic strength, the thicker the particles' diffuse layer and the more evident the effect.

Examination of Fig. 1 for systems in presence of buffer and KBr shows that the reduced specific viscosity values are much smaller than those obtained with CTAB in water alone, which is probably related to the reduction in the electroviscous effect.

Kushner *et al.* [28, 29] have carried out similar studies with sodium lauryl sulphate, dodecylammonium chloride, dodecyltrimethyl ammonium chloride and tetradecyltrimethyl ammonium chloride in water and in aqueous solutions of NaCl. Intrinsic viscosities in all four cases were observed to decrease with the initial addition of simple electrolyte, even though light scattering measurement indicated an increase in micellar molecular weight with increasing electrolyte concentration. Such behaviour is attributed to the dimunition of the electroviscous effect, which is most noticeable at low electrolyte concentrations and in absence of electrolytes. The minimum values of intrinsic visicosity for these four ionic surfactants were reported as ranging between 0.033 – 0.040 dl/g. These values were related with spherical micelles having a density of about 0.75 g/ml.

Table 1. Viscosity data of CTAB in water at 30°.

CTAB concn (g/ml x 10^3)	(C-CMC) (g/ml x 10^3)	Flow time (sec)*	Viscometer constant (CS/sec x 10^4)	η (CP)	η_{red}	Reduced specific viscosity (ml/g)
0.36446 (CMC)	–	878.16	9.181	0.80623	–	–
0.72892	0.36446	919.17	8.833	0.81190	1.00703	19.2919
1.09338	0.72892	937.60	8.706	0.81627	1.01245	17.0805
1.45784	1.09300	1016.33	8.079	0.82109	1.01843	16.8618
2.18670	1.82230	940.20	8.833	0.83047	1.03006	16.4956
2.91560	2.55120	1041.00	8.079	0.84102	1.04315	16.9136
3.64460	3.28010	1053.78	8.079	0.85134	1.05595	17.0574
4.37350	4.00960	968.80	8.833	0.85574	1.06141	15.3157
5.46700	5.10240	1071.36	8.079	0.86555	1.07357	14.4187
7.28920	6.92470	993.96	9.933	0.87796	1.08897	12.8432
9.11150	8.74700	1096.27	8.079	0.88567	1.09853	11.2644
10.93380	10.57000	977.40	9.181	0.89735	1.11302	10.9625
14.57840	14.21400	1048.20	8.833	0.92587	1.14839	10.4397
21.86760	21.50310	1068.80	9.181	0.98126	1.21710	10.0962
32.80140	32.43700	1176.92	8.833	1.03957	1.28942	8.9225

*Mean of three readings

Table 2 CMC values of CTAB measured at 30° under the conditions used for viscosity studies

CTAB solution	System: Buffer	System: KBr	System: PNPA	CMC
In water	–	–	–	$1.00 \times 10^{-3}M$
,,	–	–	+	$9.90 \times 10^{-4}M$
,,	–	$10^{-4}M$	–	$9.00 \times 10^{-4}M$
,,	–	$10^{-4}M$	+	$9.00 \times 10^{-4}M$
,,	–	$10^{-3}M$	–	$7.00 \times 10^{-4}M$
,,	–	$10^{-3}M$	+	$6.90 \times 10^{-4}M$
,,	–	$0.1M$	–	$2.00 \times 10^{-4}M$
,,	–	$0.1M$	+	$1.95 \times 10^{-4}M$
–	+	–	–	$2.00 \times 10^{-4}M$
–	+	–	+	$2.00 \times 10^{-4}M$
–	+	$10^{-4}M$	–	$2.00 \times 10^{-4}M$
–	+	$10^{-4}M$	+	$2.00 \times 10^{-4}M$
–	+	$10^{-3}M$	–	$1.00 \times 10^{-4}M$
–	+	$10^{-3}M$	+	$1.00 \times 10^{-4}M$
–	+	$0.1M$	–	$9.00 \times 10^{-5}M$
–	+	$0.1M$	+	$9.00 \times 10^{-5}M$

+ present; – = absent; (Buffer carbonate–bicarbonate, PNPA = *p*-Nitrophenyl acetate $4 \times 10^{-5}M$.

Another factor which might contribute to the relatively high η_{red} values could be assymmetry of the patrticles. Previous light scattering studies [25] show dissymmetry for this system up to around $7.5 \times 10^{-3}M$ CTAB concentration which then disappears at high CTAB concentrations.

It is evident from Figs 1–3 that for all systems studied, with the exception of those containing $0.1M$ KBr the η_{red} against micellar concentration polts are not linear. The majority have negative slopes at low values of CTAB and plateau out at high concentrations. The dashed line of the plot represents the critical region of $8.5–9.6 \times 10^{-3}M$ CTAB. Although there is not a well-defined break, it is apparent there is a change in behaviour in these concentration regions. It is also noticeable that with both aqueous and buffered solutions the difference in the plots above and below the critical region become less pronounced as KBr is added. At $0.1M$ electrolyte this difference has completely disappeared for both buffer and nonbuffer systems and straight lines with positive slopes were obtained (Figs 2 and 3). This effect should be compared with that obtained in the previous kinetic results where the addition of KBr both in buffer and nonbuffer systems gradually depresses the maximum in the SER–CTAB concentration profiles [25]. The kinetic maximum completely disappeared at $0.1M$ KBr concentration. A similar effect is also found with previous light scattering results where the biphasic character of the $\frac{H\Delta C}{\Delta\tau}$ /ΔC plot for the buffer + $0.1M$ KBr system also disappeared [25].

It is interesting to note that extrapolation of the plateau regions obtained at higher CTAB concentrations for

the buffered systems with up to $10^{-3}M$ KBr and without KBr (Fig 1) gives intrinsic viscosity values of about 4, which is not far removed from that expected for spherical particles, which correlates with previous light scattering results as dissymmetry is around unity in this region of CTAB concentrations [25]. Extrapolation from the lower concentration region yields much higher intrinsic viscosities which implies that the micelles are larger at lower CTAB concentrations. This is in direct agreement with previous light scattering results which show high aggregation numbers in the low surfactant concentration regions.

The upswing in η_{sp}/C profile at low CTAB concentration (Fig. 1) is, however, not necessarily the result of merely electroviscous effect as in the case of ionic polymers which also do not aggregate. The change in the size of the micelle in the low and higher concentration region, i.e. below and above the critical region of CTAB is made evident not only by the viscosity measurement but also by our previously reported light scattering data [31] obtained under exactly similar condition as in the present investigation. The micellar molecular weight for CTAB in water with no added salt obtained from the linear parts of the light scattering plot below the break (lower concentration region) was reported as 33500 at 30° [31], which compares with the literature values of 33000 [33], 34000 – 35000 [14] and 37000 [26]. The aggregation number obtained in this region was 104 [31].

From the linear part of the plot above the break (higher concentration region) the molecular weight was obtained as 4630 [31]; this is surprising since one might have expected the molecular weight to increase at higher concentrations. It is interesting to note that although Ekwall [14] has carried out measurements extending this range of concentrations he does not use them to calculate micellar molecular weight. His data, however, yields a value of 4600 in this region. The aggregation number calculated for this region was 13 [31].

Examination of the light scattering data presented elswhere [25, 31] also shows that the number of charges per micelle (about 13) is effectively constant below the SER maximum in the region of $8.5 - 9.6 \times 10^{-3}M$ which in light scattering experiments occurs around $1 \times 10^{-2}M$ CTAB. However, at higher CTAB concentrations the number of charges falls to 0.5 per micelle but again remains constant in this region.

Thus our previous light scattering studies on CTAB systems [25, 31] are consistent with the fact that the change in size and shape of the micelles do occur below and above the critical region of CTAB which probably would be the reason for the change in viscosity in this region too. Had there been no change in size and shape of the micelles it would have also not given two different molecular weights, charges and aggregation numbers for the same one system under examination. Thus the present study led to the conclusion, supported by previous light scattering measurement that changes in the physical nature of the micelles are taking place in the region of $10^{-2}M$ CTAB which is coincident with the maxima in the kinetic sutdies.

Further work to have more information on this critical region of CTAB is now proceeding in these Laboratories.

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