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The association parameters of bromide and iodide ions with cationic micelles using steady state fluorescence quenching measurements

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Abstract

The fluorescence quenching of 2-aminonaphthalene (2-AN) and 2-aminochrysene (2-AC) by Br^- and I^- ions was studied in different concentrations of cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) detergents. The results show that both inorganic ions are partitioned and bound to both micelles, with the exception of 2-AC where I^- ions distribute between the aqueous and micellar phases. The partition coefficients and binding constants of I^- ions in these micelles are much larger than those of Br^- ions. The decrease in the quenching rate constant (k_q) in the micelles is larger for 2-AC than for 2-AN, indicating that 2-AC is present in the micelles at a site at which the viscosity is high.

Keywords: Association parameters; Bromide ions; Iodide ions; Cationic micelles; Fluorescence quenching

1. Introduction

Fluorescence quenching by neutral or charged species has been used extensively to determine the location of probe molecules and to study the various association properties of quenchers with micelles [1–7]. This, in turn, aids in the determination of the structure of micelles. Sawer and Blatt's group [8–18] have used the fluorescence quenching of anthracene, 9-methylanthracene and *n*-(9-anthroxyl) fatty acids by dimethylaniline (DMA) and I^- ions to study the association parameters of the quenchers and the location of the probe molecules in cetyltrimethylammonium bromide (CTAB) micelles and different lipid bilayers. Their results have confirmed that water- soluble I^- ions diffuse into the micellar site where the probe molecules are located, rather than the probe molecules diffusing to the Stern layer. In other words, water molecules enter the non-polar sites of micelles and lipid bilayers.

In this study, we have investigated the fluorescence quenching of two aromatic amines (2-aminonaphthalene (2-AN) and 2-aminochrysene (2-AC)), located near the Stern layer and towards the core of the micelles respectively, by water-soluble inorganic anions (Br^- and I^-) in cetyltrimethylammonium chloride (CTAC) and CTAB. Although, qualitatively, it is known that I^- ions bind or partition to CTAC more readily than Br^- ions [19], we have attempted to determine these constants quantitatively. To establish confidence in this method, we have also carried out a study in CTAB micelles using I^- ions.

2. Materials and methods

2-AN (Riedel de Haen Seelz, Hannover), 2-AC and CTAB (Aldrich Chemical Co., UK) were purified as explained previously [20]. CTAC (Aldrich), NaI, NaCl and NaOH (AnalaR grade, BDH) were used as received. Triply distilled water was used to prepare the solutions. The pH (9 ± 0.05) of the solutions was maintained by adding a small amount of concentrated NaOH solution. This is to ensure that the aromatic amines are present in the basic form.

Absorption spectra were recorded on a Shimadzu 190UV spectrophotometer, equipped with a 135-U chart recorder. Fluorescence intensities were measured on a scanning spectrofluorometer, fabricated in our laboratory; details are available elsewhere [21]. Since most of the work involves the measurement of fluorescence

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intensities at one wavelength, no correction was applied to the fluorescence data. Fluorescence decay data were collected on an Ortec/Applied Photophysics nanosecond spectrofluorometer (model SP-70/80), using the time-correlated single-photon counting technique, and were analysed using non-linear least-squares iterative reconvolution procedures as described previously [21]. The pH values of the solutions were measured with a Toshniwal pH meter (model CL 46).

Stock solutions of 2-AN and 2-AC of concentrations 10^{-3} M were made in methanol; the final concentration of the fluorophore was 1×10^{-5} M, containing 1% (v/v) methanol. The quencher concentrations were varied between 0.01 and 0.1 M for Br^- and 0.001 and 0.01 M for I^-. The detergent concentrations were in the range 0.02–0.09 M. Under these conditions, the average number of probe molecules, even in the smallest concentration of detergent (0.02 M), does not exceed 0.04 for CTAB (aggregation number of 80) and 0.06 for CTAC [22] (aggregation number of 115). If Poisson statistics [23] are assumed, this corresponds to a probability of 2.7×10^{-4} of there being more than one probe molecule per micelle in the former case.

In all the experiments, solutions were kept at an ionic strength of 0.1, with the addition of NaCl. This is to ensure that the shape and structure of the micelles remain the same under all conditions.

3. Results and discussion

3.1. Fluorescence quenching by I^- in CTAB and CTAC

The observation of a single excited state lifetime of 2-AN and 2-AC in both detergents, even at 0.02 M, indicates that the fluorophores are present at only one site. The fluorescence quenching of 2-AN and 2-AC by I^- ions was investigated in different concentrations of CTAB and CTAC (0.02–0.09 M). I_0/I (where I and I_0 are the fluorescence intensities of the given fluorophore in a given detergent concentration with and without quencher) of 2-AC is plotted against the total quencher concentration according to the Stern–Volmer equation in Figs. 1(a) and 1(b). The Stern–Volmer equation is given by

$$\tau_0/\tau = I_0/I = 1 + k_q\tau_0[Q]_T \quad (1)$$

where k_q is the second-order quenching rate constant and τ and τ_0 are the excited singlet state lifetimes in the presence and absence of quencher. The behaviour of 2-AN is similar to that of 2-AC. The lifetimes of 2-AC in 0.045 M CTAB and 0.045 and 0.09 M CTAC were measured in the presence of different quencher concentrations. τ_0/τ vs. [Q] is also plotted in Figs. 1(a) and 1(b). The behaviour of the steady state and dynamic

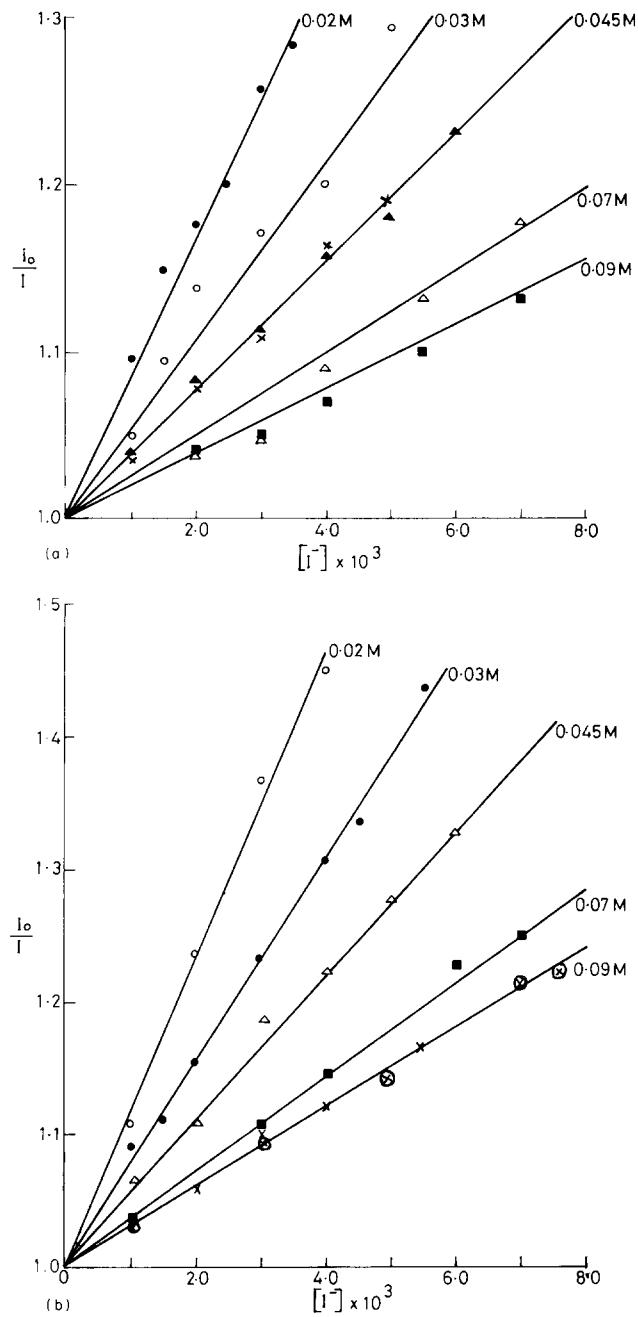

Fig. 1. (a) Stern–Volmer plots for the quenching of 2-AC by I^- ion at different CTAB detergent concentrations. The crosses indicate τ_0/τ vs. $[I^-]_T$ plot for 0.045 M CTAB. (b) Stern–Volmer plots for the quenching of 2-AC by I^- ion at different CTAC detergent concentrations. The crosses indicate τ_0/τ vs. $[I^-]_T$ plot for 0.09 M CTAC.

Stern–Volmer plots is similar, indicating that only dynamic quenching is taking place. The fluorescence quenching of 2-AN by I^- in different detergent concentrations is also similar. It is evident from the results of Figs. 1(a) and 1(b) that the fluorescence quenching efficiencies of both fluorophores decrease with an increase in CTAB and CTAC concentration. A similar

kind of behaviour has been observed previously [14,15] and clearly indicates that the quencher associates with CTAB.

The nature of the association of I^- ions with CTAB and CTAC has been determined with the help of a model suggested by the group of Blatt and Sawer [14]; in this model, the fluorescence quenching efficiency at a given quencher concentration is determined by the average number of quencher molecules per micelle ($\langle Q \rangle$). Thus the total quencher concentration is defined as

$$[Q]_T = \langle Q \rangle [Mic] + [Q]_A \quad (2)$$

where $[Q]_A$ is the quencher concentration in the aqueous phase and $[Mic] = ([Det] - cmc)/N$ where cmc is the critical micelle concentration. Fig. 2 shows a plot of $[Q]_T$ vs. [CTAB] at the same quenching efficiency for a series of values with the same I_0/I. Values of $\langle Q \rangle$ and $[Q]_A$ were determined from the slopes and intercepts respectively. The values of $\langle Q \rangle$ and $[Q]_A$ so obtained were used in a Scatchard plot (i.e. $\langle Q \rangle/[Q]_A$ vs. $\langle Q \rangle$). Fig. 3 shows such a plot for 2-AC–I^- in CTAB. A modified Stern–Volmer plot (i.e. I_0/I vs. $\langle Q \rangle$ instead of $[Q]_T$) is also given in Fig. 3.

The modified Stern–Volmer plots for both fluorophores obey a linear relationship. The values of k_q in each case were calculated from the slopes, using τ_0 and $[Q]_m = \langle Q \rangle / V_m$ where V_m is the molar volume of the respective micelles. The molar volume of CTAB is taken as 28.6 $dm^3\ mol^{-1}$. The molar volume of CTAC is assumed to be the same even though the aggregation number of CTAC [22] (115) is greater than that of CTAB (80) and thus we may expect a larger molar volume; however, this may be partly compensated by the smaller size of Cl^- in CTAC. The data are given in Table 1. Two points are worth noting. Firstly, the values of k_q observed for each quencher in the micelles are lower than those observed in pure aqueous medium [24] (4.5×10^8 and 2.8×10^8 $M^{-1}\ s^{-1}$ for 2-AN and 2-AC respectively) and, secondly, the percentage decrease in the quenching rate constant for 2-AC is higher than that observed for 2-AN. This is because the micellar phase is more viscous than the aqueous phase, and 2-AN is located near the Stern layer, whereas 2-AC is located further inside the micelles, in agreement with earlier results [20,21].

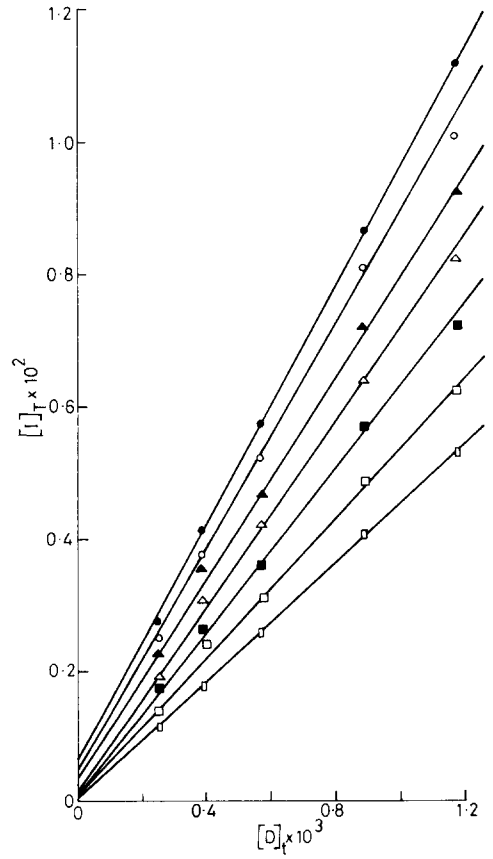

Fig. 2. Plots of $[I^-]_T$ vs. [CTAB] at the same quenching efficiency for a series of values of the same I_0/I. [2-AC] = 1×10^{-5} M.

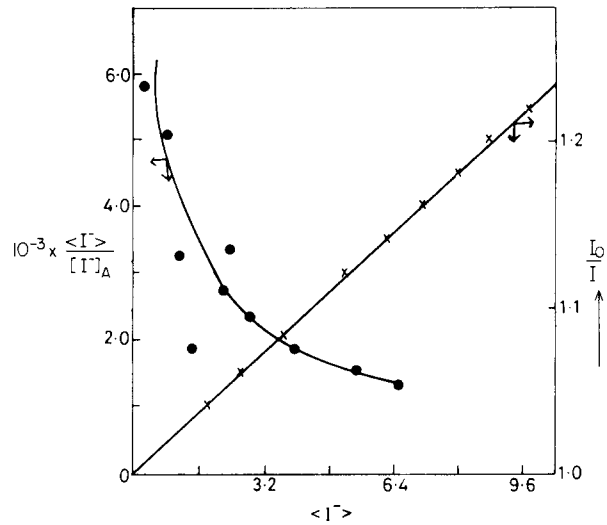

Fig. 3. $\langle I^- \rangle/[I^-]_A$ vs. $\langle I^- \rangle$ plot with I^- as quencher and 2-AC as fluorophore. I_0/I vs. $\langle I^- \rangle$ plot for the quenching of 2-AC by I^- ion.

The Scatchard plot is independent of $\langle Q \rangle$ for 2-AC–I^- in CTAC, indicating that the I^- ion partitions between the aqueous and CTAC micellar phase. An experiment carried out without keeping the ionic strength constant also gave the same results. On the other hand, the Scatchard plots of both molecules in CTAB and for the 2-AN–I^- system in CTAC are non-linear and show a decreasing dependence of $\langle I^- \rangle/[I^-]_A$ with increasing $\langle I^- \rangle$, asymptotically approaching a constant value. Since the fluorescence quenching observed in the present case is only dynamic in nature, it may be concluded that the I^- ions partition as well as bind to the CTAB micelles. This behaviour can be described by the equation [14]

$$K = \langle Q \rangle / [Q]_A = K_p V_m + p K_b / (1 + K_b [Q]_A) \quad (3)$$

Table 1
Different parameters obtained from the fluorescence quenching of 2-AN and 2-AC by Br^- and I^- in CTAC and CTAB

Compound	CTAC[a]								CTAB			
	Br^-				I^-				I^-			
	p	K_p	$K_b \times 10^{-3}$	$k_q \times 10^{-7}$ (M^{-1} s^{-1})	p	K_p	$K_b \times 10^{-4}$	$k_q \times 10^{-7}$ (M^{-1} s^{-1})	p	K_p	$K_b \times 10^{-4}$	$k_q \times 10^{-8}$ (M^{-1} s^{-1})
2-AN	12±2	63±7	1–2	1.3±0.1	2±0.25	680±30	5–6	8.0±0.2	3±0.5	330±30	2–3	1.3±0.1
2-AC	15±2	74±7	1–2	0.8±0.05	–	650±40	–	6.3±0.2	4±0.5	315±30	1.5±2	0.7±0.04

[a] Molar volume of CTAC is assumed to be 28.6 dm^3.

where K is a generalized association parameter, K_p and K_b are the partitioning and binding constants and p is the number of equivalent binding sites. The asymptotic behaviour indicates that, at this value of $\langle Q \rangle$, the binding sites are saturated and only the partitioning contribution remains. The value of the partitioning coefficient [12] is thus calculated from a plot of $\langle Q \rangle$ vs. $[Q]_A$ (Fig. 4). The values of K_p obtained from the slope and the molar volume of CTAB and p obtained from the intercept are given in Table 1. Under these conditions, the values of K_b can be calculated from Eq. (4), obtained after rearranging Eq. (3)

$$K_b = (K - V_m K_p)/\{p - [Q]_A(K - V_m K_p)\} \quad (4)$$

and using the maximum value of K and the corresponding value of $[Q]_A$. The values of K_b are very sensitive to the values of p and K and the errors observed could be ±50%. The data compiled in Table 1 give the upper and lower limits of K_b. The values of K_p obtained agree well with the literature data [17], confirming that the partitioning coefficient of I^- to CTAB is independent of the fluorophore. The value of K_p of I^- to CTAC is nearly twice as large as that to CTAB.

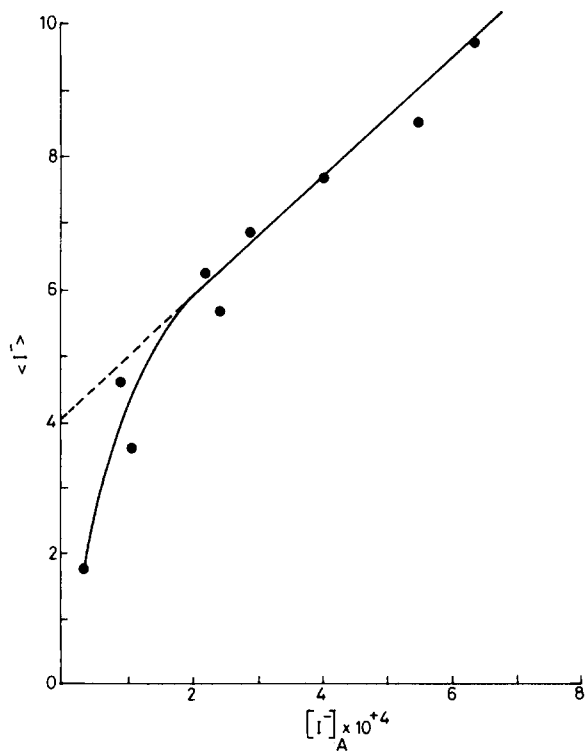

Fig. 4. Plot of $\langle I^- \rangle$ vs. $[I^-]_A$.

3.2. Fluorescence quenching by Br^- ion in CTAC

Stern–Volmer plots (I_0/I vs. $[Br^-]_T$, Fig. 5) for both the fluorophores in CTAC are different from those observed for CTAC–I^- or CTAB–I^-. The plots show a downward trend becoming parallel to the x axis. This could be due to the fact that the fluorophore may be located at two different sites and only one site is accessible to the quencher molecules, or the quenching sites available to the quencher in the micelles are saturated. The former is rejected on the following grounds: (a) only one lifetime is observed for each fluorophore in CTAC micelles and the lifetimes of both fluorophores (especially 2-AN) are sensitive to the environment; (b) the concentration of Br^- ions used is an order of magnitude greater than that of I^- and the magnitude of the slope decreases with an increase in detergent concentration; (c) a similar behaviour should also have been observed for I^- as quencher.

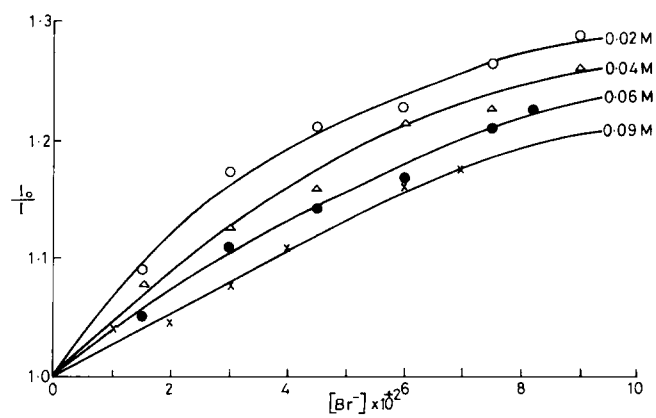

Fig. 5. Stern–Volmer plots for the quenching of 2-AC by I^- ion at different CTAC detergent concentrations. The crosses indicate τ_0/τ vs. $[I^-]_T$ plot for 0.09 M CTAC.

The Scatchard plots obtained as mentioned earlier were non-linear for both 2-AN and 2-AC. This indicates that Br^- ions bind as well as partition to CTAC. The value of K_p obtained from the linear portion of the Scatchard plot and from the plot of $\langle Q \rangle$ vs. $[Q]_A$ are not very different from each other. The values of K_p, K_b and k_q calculated in the same manner as described earlier are given in Table 1.

4. Conclusions

Our results show that K_p of I^- between CTAB micelles and water is independent of the fluorophore, and the values obtained using 2-AN and 2-AC as probe molecules agree well with literature data [17]. This confirms the accuracy of the method. The following conclusions can be drawn.

(1) The partitioning coefficient and binding constants of the Br^- ion are lower than those of the I^- ion in CTAC micelles; the I^- ion has a strong affinity for the micellar interior in comparison with Br^-. This is expected because the I^- ion is larger than the Br^- ion and can be easily polarized, i.e. the former ion is more hydrophobic and thus is soluble in less polar environments. Earlier work in the literature also suggests similar results [19].

(2) The relative decrease in the value of k_q in comparison with that in aqueous medium for 2-AC is larger than that obtained for 2-AN. This indicates that, in micelles, 2-AN is located near the Stern layer, whereas 2-AC is located in a more viscous environment. As expected, this effect is stronger for Br^- than for I^-. Our earlier observation [21] that the excited singlet state lifetime of 2-AN decreases, whereas that of 2-AC remains constant, with an increase in CTAB concentration confirms this observation.

(3) Regarding the penetration of water-soluble anions into the interior of the micelles, we agree with the model proposed by Menger and coworkers [25–28] (i.e. micelles are viewed as a loosely packed and disordered structure containing large irregularities which are filled with water), although other models have also been proposed [29–34] for the structure of micelles. In other words, the Br^- and I^- ions diffuse to the site of the fluorophore present in the micelles and quench the fluorescence, rather than the fluorophore diffusing to the quencher in the bulk aqueous medium, because the lifetimes of the fluorophores (especially 2-AC) are too small to reach the Stern layer from inside the micelles. A similar behaviour has also been observed previously [29,30]. Menger's model is also consistent with earlier results [21], i.e. the large Stokes' shifts $\{\bar{\nu}_{max} - \bar{\nu}_{flu}\}$ observed for aromatic amines in CTAB and CTAC can be explained only if protic environments are present around the aromatic amines in micelles.

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