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Detection of tight ion-pair in some novel lipopathic oxidants from the monolayer at air-water interface

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From the isotherms of surface pressure and area of cetyltrimethylammonium dichromate, permanganate and ceric nitrate, the anchoring area on water-air interface for each oxidant has been determined by spreading as Langmuir monolayer. The area/molecule of these oxidants with a common amphiphilic counterion, i.e., cetyltrimethylammonium ion, depends on the size of the anion counterpart indicating the existence of contact ion pair between CTA^+ and the anionic group in aqueous medium. However, in aqueous acetic acid subphase, the decrease in area/molecule of cetyltrimethylammonium dichromate indicates dissociation of the constituting ions.

Keywords: Solution chemistry, Ion pairs, Tight ion pairs, Water-air interface, Anchoring area, Monolayer properties

An onium ion, as the counterion for anionic oxidants such as Mn(VII), Cr(VI), Ce(IV) etc., makes a significant difference in oxidation potential of the oxidant as well as to the oxidizing system. It makes the oxidant lipid soluble, mild, and many a times, chemoselective. Tailor-made oniums have been used as counterions wherein, heterocyclic bases such as pyridine, quinoline, caffeine, imidazole and nicotine units become a part of the oxidant[1]. In different reaction conditions, these oxidants often show biomimetic characteristics. This is due to the counterions, which provide micro-heterogeneous environments with different solubilization pockets for the substrates, as in the case of micelles, reversed micelles, microemulsions, vesicles for artificial systems and proteins and lipid membranes in living systems. Among these oxidants, Mn(VII)[2] and Cr(VI)[1] have been studied extensively.

Symmetrical tetraalkylammonium ions are mostly used as lipopathic carriers of the lipophobic counterions[3]. Cetyltrimethylammonium ions (CTA) having a point charge and capable of forming organized assemblies in both aqueous and nonaqueous media have also been used for converting the oxidants to lipopathic[4]. Dash and Mishra[5] have reported the product specificity of cetyltrimethyl-ammonium permanganate (CTAP) in chloroform medium for olefinic double bonds. The *cis* compounds are converted to the corresponding diols, whereas the *trans* compounds lead to cleavage of the double bond. They have proposed a mechanism for the self-oxidation of CTAP in chloroform akin to β-oxidation of fatty acids by the corresponding dehydrogenase[6]. This mechanism is based on the existence of tight ion pair in CTAP. Patel *et al.* [7] have synthesized a lipopathic oxidant, cetyltrimethyl-ammonium dichromate (CTADC), and have investigated the oxidation behavior towards various organic substrates. CTADC is found to be milder than other Cr(VI) oxidants. In the absence of acid, CTADC exhibits some bizarre reactions with nonconventional products. Aromatic amines are found to yield the corresponding diazo compounds, while arylaldoximes yield the corresponding nitriles[8,9]. Further, in an oxidation reaction of cholesterol with CTADC, Patel and Mishra[10] have observed that 7-dehydrocholesterol is obtained instead of cholestenone. This dehydrogenation is a rare event in Cr(VI) oxidation studies, and is explained through a remote functionalization mechanism. In this mechanism, the cetyltrimethylammonium ion provides a conducive environment for proper orientation of the oxochromium group, which is also due to the tight ion pair of dichromate and onium ion, so that the removal of hydrogen becomes easier. Further, the protonated dichromate oxidizes the secondary hydroxy group of cholesterol to the corresponding ketone on the addition of acid. The reaction kinetics reveals that the reaction system resembles that of cholesterol oxidase, which carries FAD as the dehydrogenating agent in the enzyme and oxidizes cholesterol to the corresponding cholestenone. In an analogy to this system, CTADC in an organic solvent like DCM forms reversed micelles where the dichromate is

encapsulated by the cationic oniums and cholesterol is partitioned into the mesophase. The variance in oxidizing activity of these anionic oxidants having long chain cetyltrimethylammonium counterion is attributed to the formation of tight ion-pair, due to which these oxidants provide micro heterogeneous phase for the encapsulation of the organic substrates[11].

Tight ion pairs play a key role in anion and ion-pair receptor chemistry[12] and, in general, in the functional behavior of most of the anionic cofactors and substrates involved in biological transformations[13]. For the transportation of potassium through biological membrane, the role of tight ion pair is well established[14]. The stabilization of some diacids[15] and the anion-templated assemblies of catenanes and pseudorotaxanes[16] have also been supported by ion-pair mechanism. The formation of tight ion pairs depend on headgroup structure (e.g. size), counterion type, and the stability of the hydrated tight ion pair[17]. In the present study, we have made an attempt to find evidence for existence of tight ion pairs of CTA ion and the counter ions in CTAP, CTADC and cetyltrimethylammonium ceric nitrate (CTACN).

Experimental

The chemicals used for the synthesis in the present study were of high purity and were obtained from E. Merck, Sisco Chem and CDH, India.

Cetyltrimethylammonium ceric nitrate (CTACN) was synthesized as follows (Eq. 1)[18]: Ceric (IV) ammonium nitrate (CAN: 5.5 g, 0.01 *M*) in 10 mL water was added slowly to an aqueous solution to cetyltrimethylammonium bromide (10.3 g, 0.03 *M*) with continuous stirring on a magnetic stirrer. A yellow compound appeared slowly. Stirring was continued for 30 minutes after completion of addition of CAN. The resulting yellow compound was filtered off and washed with chilled water several times till no trace of bromide was detected in the filtrate. It was vacuum dried and kept in a dark bottle inside a desiccator. M.pt.: 91°C; Yield: 90%; C, 42.17%; H, 7.52%; N, 14.0%; $C_{38}H_{84}N_8O_{15}Ce$ requires C, 42.22%; H, 7.77%; N, 13.73%. IR (in cm^{-1}) 2990, 2860, 1450, 1305, 1030, 950, 900, 812, 722.

$$2C_{16}H_{33}N^+(CH_3)_3Br^- + Ce(NH_4)_2(NO_3)_6 \rightarrow [C_{16}H_{33}N^+(CH_3)_3]_2Ce(NO_3)_6^{--} + 2\,KBr \quad \ldots (1)$$

Cetyltrimethylammonium permanganate[7] was prepared by stirring cetyltrimethylammonium bromide with an equivalent amount of potassium permanganate in distilled water (Eq. 2). A dark compound separated out immediately, which was washed with water several times. The compound decomposed at 98°C inside a capillary tube and exploded violently in the temperature range of 115- 120°C when heated on a wider surface, (Yield: 92%).

$$C_{16}H_{33}N^+(CH_3)_3Br^- + KMnO_4 \rightarrow [C_{16}H_{33}N^+(CH_3)_3]\,MnO_4^- + KBr \quad \ldots (2)$$

Cetyltrimethylammonium dichromate[8] was synthesized by treating potassium dichromate in aqueous solution of cetyltrimethylammonium bromide (Eq. 3). The insoluble salt was isolated, made free from excess CTAB and potassium dichromate by washing with water for several times. It was vacuum dried and kept in a dark bottle inside a desiccator. M.pt:. 212°C, Yield: 98%; C, 58.14%; H, 10.65%; N 3.54%; Cr, 13.11%; $C_{38}H_{84}O_7N_2Cr_2$ requires C, 58.16; H, 10.71; N, 3,57;Cr, 13.26%. IR (in cm^{-1}) 771, 879, 933, 1467, 2850, 3028, 3471.

$$C_{16}H_{33}N^+(CH_3)_3Br^- + K_2Cr_2O_7 \rightarrow [C_{16}H_{33}N^+(CH_3)_3]_2Cr_2O_7^{--} + KBr \quad \ldots (3)$$

The NMR spectra for CTAB, CTACN, CTAP and CTADC were recorded on Jeol-400 MHz in $CDCl_3$.

All monolayer experiments were performed with a computerized Langmuir-Blodgett trough system developed by Apex Instruments Co. at IACS Kolkata. The instrument, a dual trough system, consisted of a teflon trough with a deeper well for dipping. The working area was maintained by a continuous perimeter PTFE (polytetraflourothylene) coated glass fiber barrier. Triply distilled deionized water was used as the sub-phase.

A known quantity of the solution of the amphiphiles in dichloromethane (1 mg mL^{-1}) was spread slowly on the sub-phase by means of a microsyringe so that a uniform monolayer was formed. Surface pressure/area isotherms were recorded at a barrier speed of 2 cm^2 min^{-1}. All pressure/area isotherms are the average of triplicate runs. The reproducibility, at a given surface pressure, was within the error of ± 0.5 A^2/molecule.

For the determination of monolayer stability, the monolayer was compressed up to the collapse and at that point it was allowed to rest. The surface pressure did not change by more than 0.1 mN/m in 2h.

Results and discussion

Amphiphilic compounds can form monolayer at water/air interface. Cetyltrimethylammonium bromide is an established amphiphilic compound with almost equal solubility in water and chloroform. The Hydrophilic Lipophilic Balance (HLB) is an indicator of amphiphilic characteristics. Davies[19] has proposed a numeric value to determine the HLB for amphiphilic compounds with different constituting functional groups. Cetyltrimethylammonium ion has a HLB value of 8.8 and is capable of forming both micelles and reversed micelle in aqueous and nonaqueous medium respectively. Senapati *et al.*[20] have reported the formation of reversed micelle of CTAB in chloroform medium. Thus, CTAB can also form monolayer on water surface but with poor stability.

The counterions contribute significantly to the solubility of ionic amphiphiles. Quaternary ammonium ions form contact ion pairs with the counter ions[3d] and increase the solubility in organic solvents, and correspondingly, the solubility decreases in aqueous medium. The extent of solubilization contributes to the partitioning of the molecules between surface and bulk and, thus, to the formation of monolayer on the water surface. With a view to study the effect of counter ions on the formation of monolayers, bromide of CTAB was exchanged with large counter ions such as dichromate, permanganate and ceric nitrate. Earlier, Lissi *et al.*[21] have reported a successful method for the exchange of bromide by hydroxyl, fluoride, chloride, nitrate and perchlorate ions and have investigated their aggregation behaviour in aqueous medium. The exchange of counter ions, in the present study, is found to change the solubility significantly. CTACN is sparingly soluble in water and in many polar organic solvents, and insoluble in non-polar solvents like hexane, benzene and toluene. CTAP and CTADC are found to be almost insoluble in water but soluble in all organic solvents. The elemental analyses of these compounds reveal that both the dichromate and ceric nitrate carry two cetyltrimethylammonium ions each.

The NMR spectra for CTAB, CTACN, CTAP and CTADC were recorded in $CDCl_3$ and the chemical shift values assigned to different protons of CTA are presented in Table 1. The analysis of the NMR data clearly shows that there are significant changes in the chemical shift values of $N(CH_3)_3$ and α-CH_2- with change in counter ions while almost no changes have been observed in other protons. These oxidants exist as ion pairs in organic solvents and the protons close to the counter ions suffer significant changes in chemical shift values compared to other protons. Changes in chemical shift values of protons in trimethyltetradecylammonium bromide have been analysed to probe the binding/incorporation of fluorobenzoates by Vermathen *et al.*[22] They observed shifting of chemical shift for the terminal protons, i.e., $-N(CH_3)_3$ and ω-CH_3, by the same magnitude and proposed the incorporation of the benzoate ion into the micelle.

With a view to investigate the effect of counter ion on the surface area of CTAB, CTAP, CTADC and CTACN, the π-A isotherms were constructed (Fig. 1). When dichloromethane solution of CTAB was spread on the water surface and the surface pressure was plotted against area/molecule, the isotherm thus obtained was with almost no liquid phase. A condensed state was obtained at a surface area/molecule of 20 $Å^2$. In the condensed monolayer

Table 1—Chemical shift values (δ) of different protons of CTAB, CTACN, CTADC and CTAP in $CDCl_3$

	Chemical shift (δ)				
	$-N(CH_3)_3$	α-CH_2-	β-CH_2-	$-(CH_2)_{13}$	ω-CH_3
CTAB	3.35	3.58	1.72	1.21	0.82
CTACN	3.33	3.50	1.72	1.26	0.88
CTADC	3.42	3.51	1.74	1.26	0.86
CTAP	3.11	3.30	1.75	1.28	0.89

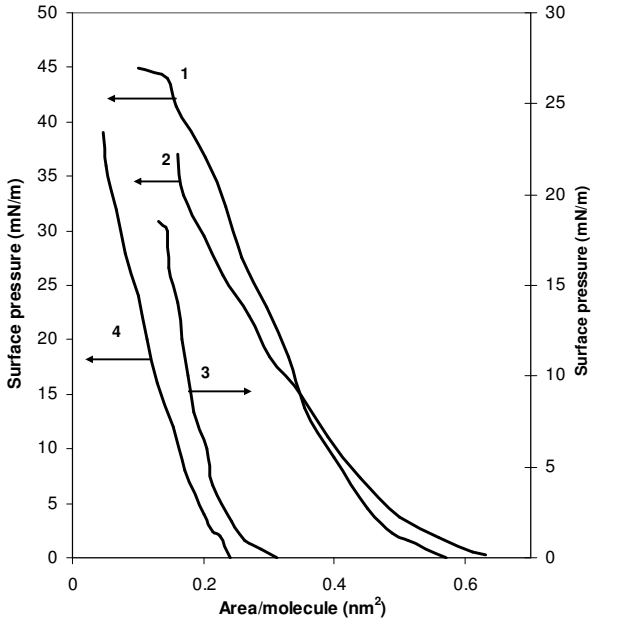


Fig. 1—Surface pressure versus area curve on water subphase. [1, CTACN; 2, CTADC; 3, CTAP; 4, CTAB].

state, the packing of the molecules contributes to the area/molecule. Earlier, from a large number of experiments on fatty acids, Alexander[23] concluded that the monolayer films of the acids with 19-21 $Å^2$ are due to close packed vertically oriented methylene chains, which may be applicable to CTAB in the present case.

Similar monolayer spreading of CTAP, CTADC and CTACN in dichloromethane medium were carried out at the air/water interface and the respective surface area/molecule values were determined to be 22, 51 and 45 $Å^2$. It indicates that the surface area value of CTAP is due to a single cetyl chain, while the values for CTADC and CTACN are due to two cetyl groups. Considering the formation of condensed monolayer for the species and the surface area for a single cetyl chain being 20 $Å^2$, the change in surface area/molecule is due to the difference in size of the counter ions. The counter ion size increases in the order: $Br^- < MnO^{4-} < [Ce(NO_3)_6]^{2-} < Cr_2O_7^{2-}$, which is reflected from the corresponding increase in surface area/molecule. From the surface potential-time plots, the monolayers of these compounds are found to be stable, suggesting the existence of tight ion pair in the compounds.

In a double tailed surfactant, the area/molecule is due to the cumulative cross sectional area of the hydrophobic tails and small counter ions forming tight ion pair should decrease the area/molecule. From the investigation of the area/molecule of dioctadecyldimethylammonium methacrylates on water surface, Fukuda *et al.*[24] observed a decrease in the area/molecule by replacing the bromide ion by methacrylates and established the existence of ion pair in the molecule.

With a view to investigate the effect of acid on the ion pair of CTADC, acetic acid was added to the sub-phase and the π-A isotherms were constructed (Fig. 2). The presence of acetic acid in the aqueous sub-phase does not influence the shape of the π-A isotherms. However, with increasing acid concentration, the contraction of the monolayer on the sub-phase increases and thus the area and the surface pressure decrease. This decrease reflects the increasing interaction of acetic acid with the dichromate ion to form a protonated dichromate, which leads to dissociation of the CTA^+ ion and the dichromate (Scheme 1). Protonated dichromate, being soluble in water, partitions into the bulk with a decrease in the anchoring area of the molecule on

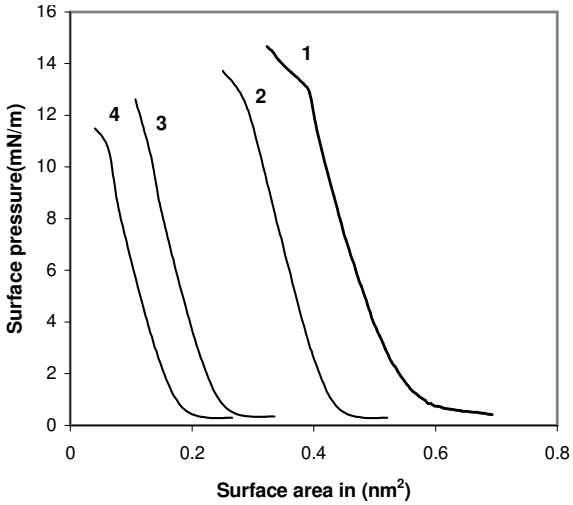
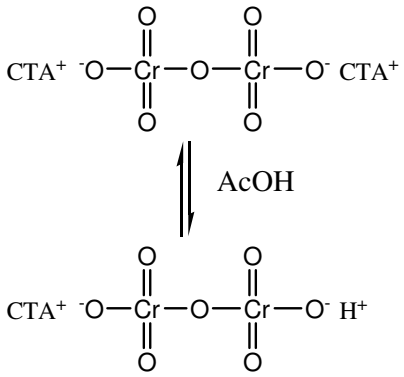


Fig. 2—Plot of surface pressure versus area of CTADC at different acetic acid concentrations. [1, 0.18 *M*; 2, 0.22 *M*; 3, 0.45 *M*; 4, 0.51 *M*].



Scheme 1

water surface. The decrease is found to be asymptotic and the minimum area is comparable to the area of CTAB as monolayer. Due to the strong reactivity of CTACN and CTAP with acetic acids, similar studies could not be undertaken.

The present study shows that the tight ion pairing of counter ions in the amphiphilic oxidants affects the solubility, NMR spectral characteristics of proximal protons and also the surface-area/molecule on air-water interface. The lipopathic oxidants, CTAP, CTACN and CTADC exist as tight ion pairs forming stable monolayers at air-water interface. With increase in the size of the counterions the area/molecule value also increases. These stable monolayers can be transferred to inert solid matrix for probable applications in solid phase oxidation process.

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