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Surface Tentiometric Studies on the Interaction of Anionic Polyelectrolytes with Cationic Surfactants

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The interaction of cationic surfactants, n-alkyltrimethylammonium bromide (C_nTAB; n = 12, 14, 16) with anionic polyelectrolyte, poly(styrenesulfonate) (PSS) has been studied by surface tension measurement. In the absence of added salt, the cationic surfactants bind to PSS quantitatively up to ca. 60% coverage of anionic sites of the polyanion and the complexes were surface inactive. Further binding of the surfactant cations on PSS caused a sharp conformational transition of the surfactant/PSS complexes to surface active complexes and accompanied precipitation. The binding showed a biphasic behavior in the presence of NaCl and cooperativity of the binding became less as the concentration of NaCl increased. Binding of the cationic surfactants on poly(vinylsulfonate) also showed the biphasic behavior and the cooperativity of the binding was much less even in the absence of NaCl. The binding of surfactant to PSS provided hydrophobic environment to solubilized pyrene and reduced the viscosity of the solution greatly even at surfactant concentrations well below cmc. This study indicated that the surfactant bound to PSS up to 60% coverage of PSS sites are present as surfactant aggregates which are wrapped up with PSS chains, and hydrophobic interaction is an important factor in the binding of the surfactants to PSS.

Introduction

The interaction between polymers and surfactants is of great interest from the fundamental standpoint of obtaining informations on the nature of the polymer/surfactant aggregates, and also from the point of practical uses of the systems in which polymers and surfactants are utilized conjointly.[1] Extensive works have been performed on polymer/surfactant systems using a variety of technigues.[2-22] From these studies, it has been found that strength of binding of ionic surfactants on dissolved polymers depends strongly on properties of the polymers and the surfactants.

Most of works on the polymer–surfactant interaction have been conducted with neutral polymers. These include poly(ethylene oxide),[2-9] poly(N-vinylpyrrolidone)[2,6,11-13] and poly(ethylene glycol).[12,14] An anionic surfactant, sodium dodecylsulfate (SDS) was mainly used in these investigations. Neutral polymers and ionic surfactants form complexes of polyelectrolytic character, but interaction between them is weak and is believed to be mainly hydrophobic.

There are also reports on the studies on interaction between ionic polymers and ionic surfactants or hydrophobic ions of opposite charge.[5,15-22] The ionic polymers investigated include poly(styrenesulfonate)[5,15,17], poly(vinylsulfonate)[18], poly(methacrylate)[19] and polypeptides.[20-22] Luminescent probed methods[5,17,19] and potentiometry[15,16,18,20,21] using surfactant sensitive electrodes were main tools for the studies. Since polyelectrolytes interact strongly with oppositely
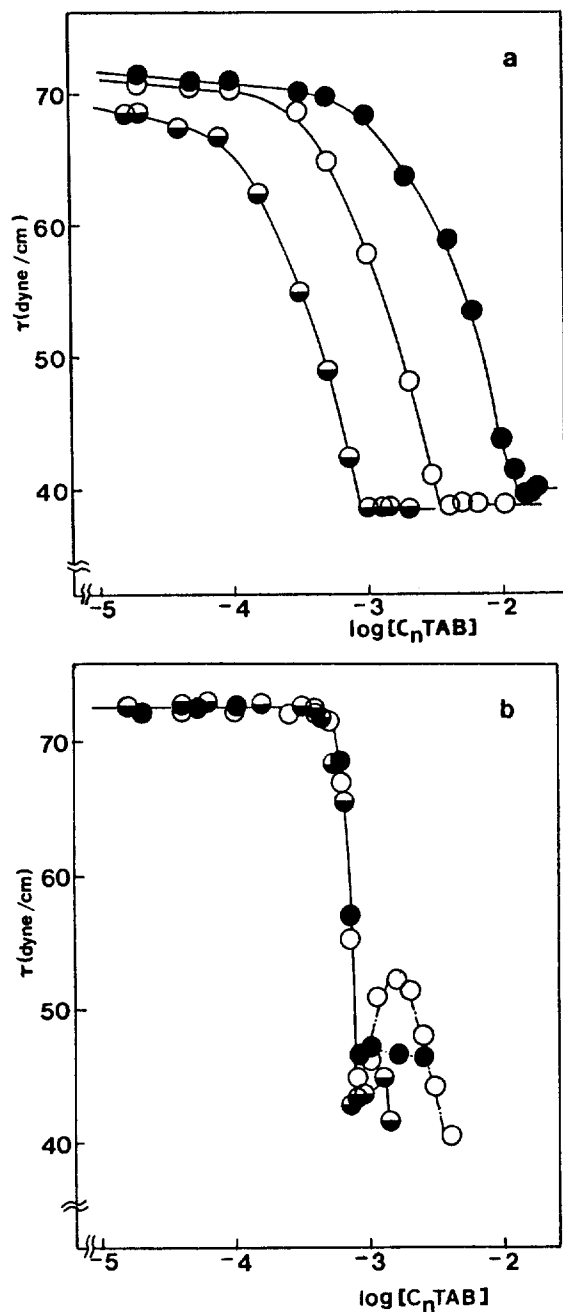
charged surfactants due to coulombic force, drastic changes in properties of polymers upon binding with surfactants are expected. Moreover, synthetic polyelectrolytes are highly simplified analogues of biomacromolecules, and the binding study of the polyelectrolytes with surfactants is expected to give informations on the formation and physico–chemical properties of biomembranes.[23]

Poly(styrenesulfonate), PSS, contains both hydrophobic phenyl moiety and hydrophilic sulfonate group. This ionic polymer can interact with cationic surfactants by hydrophobic as well as electrostatic forces. This resembles the interaction of many biological macromolecules.

In this paper, we describe results of surface tensiometric investigation on the interaction of PSS with alkyltrimethylammonium salts. The effects of hydrocarbon chain length of the surfactants and salt on the interaction were examined. The results were also compared with those on poly(vinylsulfonate)/surfactant systems.
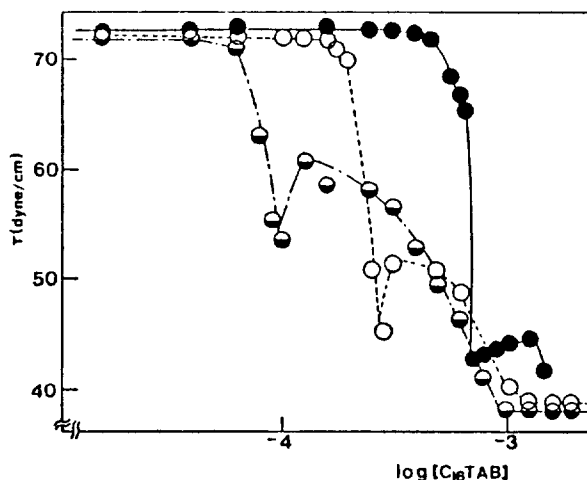
Experimental

Sodium salt of poly(styrenesulfonate), PSS, was purchased from Aldich and purified by reprecipitation from water by the addition of isopropyl alcohol. Molecular weight of PSS was determined from the intrinsic viscosity of the polymer in 0.05 M aqueous NaCl solution using the reported Mark–Houwink relationship,[24] $[\eta] = 1.39 \times 10^{-4} \times Mw^{0.72}$, of the polymer. Molecular weight of PSS was measured as 2.2 ×

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Figure 1. Dependence of surface tension of solutions on the concentrations of C_nTAB in the absence (1a) and in the presence of 1.0 mM PSS (1b) at 25 °C: $C_{12}TAB$ (●); $C_{14}TAB$ (○); $C_{16}TAB$ (◒). No other salt was added to the solutions.

Figure 2. Variations of surface tension of PSS solutions with concentrations of $C_{16}TAB$ at 25 °C in salt-free solutions. Concentrations of PSS were 0.10 (◒), 0.30 (○) and 1.0 mM (●).
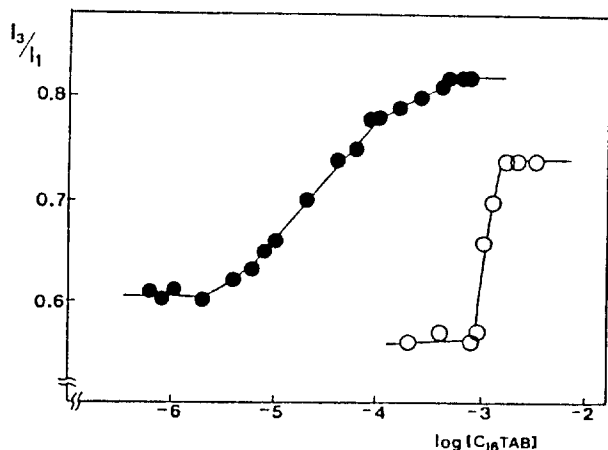
Noüy type surface tensiometer (Fisher Model 21) at 25 ± 0.2 °C. Temperature of the solutions was maintained constant by water-circulation through the jacket of the sample container. Prior to measurement of surface tension, the solutions were equilibrated for at least two hours.

Fluorescence Spectra of solutions containing pyrene were recorded on a Hitachi 650-10S spectrofluorimeter at 25 °C. The excitation wavelength was 332 nm and emission slit width was 2 nm.

Viscosity Measurements were performed with an Ubbelohde type viscometer at 25 °C. The flow time of water of the viscometer was 17.7 sec.

Results and Discussion

Surface tension (γ) of alkyltrimethylammonium bromide (C_nTAB, n = 12, 14, 16) solutions in the absence and presence of 1.0 mM PSS was measured as functions of the concentration of the surfactants. The results were presented in Figure 1. The pattern of γ *vs* log [C_nTAB] curves in the absence of PSS is typical of that observed with surfactant solutions. The concentration at inflection point corresponds to the critical micelle concentration (cmc) of the surfactant. The values of cmc were 0.90 mM for $C_{16}TAB$, 3.6 mM for $C_{14}TAB$ and 14.1 mM for $C_{12}TAB$. The presence of PSS in the solutions resulted in a large modification in the surface tension *vs* log [C_nTAB] behavior as can be seen by comparing Figure 1b with Figure 1a. When the cationic surfactants C_nTAB in concentration below 0.6 mM were added to 1.0 mM PSS solutions, surface tension of the solutions was virtually unchanged from the value of pure water (PSS did not show any appreciable surface activity in water). Surface tension of the PSS solutions dropped sharply when the concentration of C_nTAB exceeds 0.6 mM. More concentrated C_nTAB solutions caused a slight increase and then decrease in surface tension. These were illustrated in Figure 1b. Floating aggregates which are believed to be stoichiometric complexes between the surfactants and PSS were visible after the sudden drop of surface tension. The amount of the aggregates was greatest at equivalent concentration of the surfactants, 1.0 mM.

10^5. Sodium salt of poly(vinylsulfonate), PVS, was obtained as 25% (w/v) suspension from Polyscience and recovered as solid by the procedure described in a previous paper.[25] Cetyltrimethylammonium bromide ($C_{16}TAB$) was obtained from Aldrich and was recrystallized three times from ethanol. Dodecyltrimethylammonium bromide ($C_{12}TAB$), tetradecyltrimethylammonium bromide ($C_{14}TAB$) and pyrene were purchased from Aldrich and were used as received. The concentration of polymers in solutions was expressed in terms of the concentration of monomeric units. Deionized glass-distilled water was used.

Surface Tension of solutions was measured with a Du

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Figure 3. Dependence of I_3/I_1 ratio of pyrene fluorescence as functions of concentrations of $C_{16}TAB$ in the absence ($\bigcirc$) and in the presence of 1.0 mM PSS ($\bullet$).

Figure 2 shows the plots of surface tension against log $[C_{16}TAB]$ at three different concentrations of PSS. When the concentration of $C_{16}TAB$ was lower than the concentration at which surface tension of the solutions started to rise after sudden drop, the surface tension *vs* log $[C_{16}TAB]$ profiles could be virtually superposed by the parallel translation of the curves along the axis of log $[C_{16}TAB]$. The onset of sudden drop of surface tension after the long plateau was observed when the concentrations of the cationic surfactants reached about 60% of that of PSS, regardless of concentration of PSS.

The lack of any influence of added cationic surfactants on the surface tension of solutions containing PSS in the flat region suggests that the surfactants are effectively removed from the bulk solutions by quantitative binding to PSS. The binding proceeds up to 60% coverage of the anionic sites of PSS. This agrees fairly well with reports of quantitative binding of $C_{12}TAB$ on PSS up to 50% coverage made by Hayakawa and Kwak from potentiometric titrations[15,16] and by Abuin and Scaiano[17] from an ANS probed study. This suggests the extreme cooperativity of the surfactant binding on PSS in the salt-free solutions.

Remarkable cooperativeness is a general character of surfactant ions binding on polyions. The binding of inorganic counterions on the polyions shows anticooperatively,[26] presumably due to reduced electrostatic force as the binding takes place. Therefore, it appears that the binding of surfactant ions on polyions takes place not only by electrostatic force but also by hydrophobic interaction between the bound surfactant ions. The latter interaction results in formation of surfactant aggregates in the domain of the polyions. The aggregates have been referred to as "micelle-like"[20] or "mini-micelle".[17] It is clear from Figures 1b and 2 that the binding constant of a surfactant ion on an isolated site of PSS is too large and the cooperativity of the binding is too strong to reveal the difference in the lengths of alkyl chains of surfactant ions (Figure 1b) and concentrations of PSS and surfactants (Figure 2).

Figures 1b and 2 also show that the cationic surfactants/ PSS complexes of $[C_nTAB]/[PSS] < 0.6$ do not exhibit any appreciable surface activity in the salt-free solutions. This implies that the hydrophobic hydrocarbon chains of the sur-

factant ions bound to PSS are not exposed to bulk water. This can be possible by the coiling of the polyelectrolyte chains around the surfactant aggregates. This explanation is consistent with an observation of sharp decrease in viscosity of PSS solutions upon addition of $C_{12}TAB$, as compared to the addition of $(CH_3)_4NBr$.[17]

Formation of surfactant aggregates accompanying coiling of the polyelectrolyte chains was also confirmed from a pyrene probed luminescence study. It is well known that the ratio of fluorescence intensities of the third and the first vibronic peaks (I_3/I_1) of pyrene varies sensitively with micropolarity of medium where the probe molecule resides.[27] Figure 3 shows dependence of the ratio of the fluorescence intensities of pyrene in PSS-free and 1.0 mM PSS solutions on the concentration of $C_{16}TAB$. In the absence of PSS, the I_3/I_1 ratio remained low up to cmc of $C_{16}TAB$, above which it increased sharply with the concentration of the surfactant reflecting solubilization of pyrene in the hydrophobic region of the micelle. In contrast to this, the ratio started to increase with concentration of $C_{16}TAB$ far below cmc of the surfactant in the presence of PSS. This is an indication of formation of surfactant aggregates which behave as micelle to the hydrophobic solute at concentrations well below cmc of the surfactant.[17]

The drastic decrease in surface tension of PSS solutions when the concentration of surfactant exceeds about 60% of that of PSS is of particular interest. One of possible explanations for this is that the cationic surfactants bind to only ca. 60% of anionic sites of PSS, possibly by steric reason. In this case, addition of surfactant exceeding the binding capacity of PSS would increase the concentration of free surfactants and thus decrease surface tension. However, this cannot explain the increase of the surface tension observed after the sudden drop of surface tension with increasing concentration of the surfactants. Also the dependence of surface tension on the concentration of surfactants, especially in solutions of lower concentrations of PSS, is too large to account for contribution from free surfactants. The other plausible explanation is conformational change of PSS/surfactant complexes. The coiled structure of PSS might accommodate surfactant cations as aggregates (wrapped up with the polymer chain) only up to 60% of the anionic sites of the polymer. Further binding of surfactant cations would take place on the anionic sites exposed to bulk water. This could destabilize the structure of surfactant/PSS complexes adapted up to coverage of 0.6 and induce conformational transition in the backbone of the polyelectrolyte. In fact, we observed slight increase in the viscosity of the PSS solution in the surfactant concentration region where the surface tension decreases sharply (data not shown). This suggests that the conformational transition involves uncoiling of the polymer chain. Conformational transition of polymers upon surfactant binding was reported for poly(L-arginine)[22] and poly(L-ornithine) homologs[20] from coil to helix, and for poly(L-histidine)[22] from coil to β-structure by sodium dodecylsulfate. Also it was found that poly-(L-glutamic acid) adopts helical conformation in solutions of decylammonium chloride.[21] In all of these cases, conformational transition of the ionic polypeptides upon binding of oppositely charged surfactant ions was observed in narrow range of binding coverage.

If above mentioned conformational change indeed occurrs
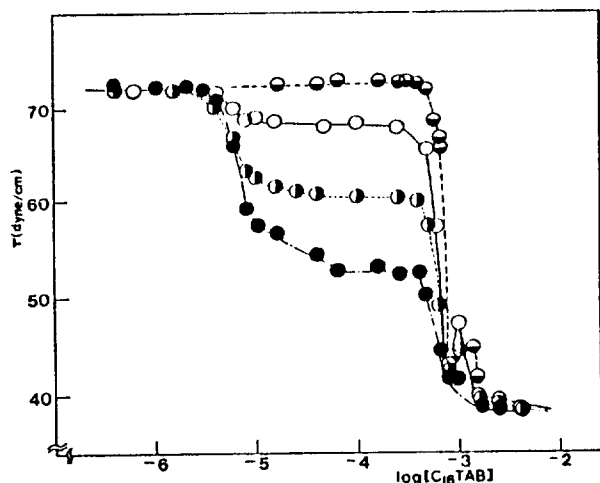
Figure 4. Plots of surface tension of 1.0 mM PSS solutions as functions of [C_{16}TAB]. Concentrations of NaCl were 0.0 (◒), 0.010 (○). 0.03 (◑) and 0.10 M (●).

Figure 5. Dependence of surface tension of 1.0 mM PVS solutions as functions of concentrations of C_nTAB in salt-free solutions: C_{12}TAB (●); C_{14}TAB (○); C_{16}TAB (◒).

in the present systems, the surfactant/PSS complexes of the newly adapted conformation should be surface active as suggested by the sharp drop of surface tension of solutions. Also, it appears that more surfactant ions can bind to the complexes of the new conformational state. This can explain the increase of the surface tension after the sudden drop of it. When the anionic sites of PSS are nearly saturated with surfactant ions by further binding, the surfactant/PSS complexes bear little net charge and are insoluble in water producing floating aggregates. At this point, added surfactant molecules would fill unoccupied sites on the solution–air interface resulting in decrease of the surface tension, and finally the surface tension of the solutions approaches to the values of pure surfactant micellar solutions.

Figure 4 shows dependence of surface tension of 1.0 mM PSS solutions on the concentrations of C_{16}TAB at various concentrations of NaCl. In contrast to the behavior in salt–free solutions, the surface tension of PSS solutions decreased progressively as C_{16}TAB in the concentration below 1.0×10^{-5} M was added to the solution in the presence of NaCl. However, in the C_{16}TAB concentration range, surface tension of PSS solutions was higher than that of PSS–free solutions at the corresponding concentrations of NaCl and C_{16}TAB. These results indicate that binding of C_{16}TAB on PSS is not quantitative, but considerable fraction of added C_{16}TAB binds to PSS in that concentration range of the surfactant in the presence of NaCl. This can be regarded as an indication of absence or weakness of cooperativity of the binding. Reduced electrostatic interaction betwen the polyanion and the surfactant cation due to increased ionic strength of the medium might be responsible for this.

More concentrated C_{16}TAB solution caused little (when [NaCl] was low) or only slight (when [NaCl] was high) decrease in the surface tension until the concentration of C_{16}TAB was ca. 0.6 mM. Again, the surface tension of the 1.0 mM PSS solutions started to decrease sharply at surfactant concentration of 0.6 mM as in the salt–free solutions. This implies that the conformational transition of PSS induced by surfactant binding is affected little by ionic strength of the medium, but the extent of PSS sites by surfactant molecules is a critical factor for the transition. The
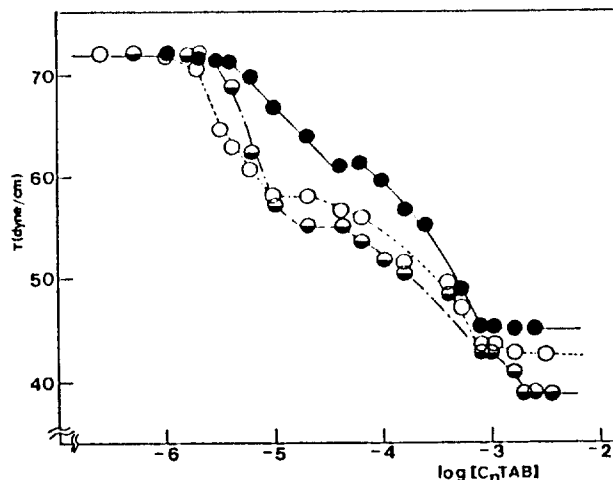
latter supports our explanation that the conformational transition of PSS/C_nTAB complexes is induced by the binding of surfactant ions to sulfonate groups exposed to bulk water in coiled structure in which only 60% of the anionic groups is accommodated inside the coil.

The biphasic binding of C_{16}TAB on PSS in the presence of NaCl, *i.e.*, weak or noncooperative binding at [C_{16}TAB]< 1×10^{-5} M and strong cooperative binding at [C_{16}TAB]>1 × 10^{-5} M, was also observed with C_{12}TAB and C_{14}TAB. The cooperativity in binding became less as the concentration of NaCl was increased. This agrees well with a report of potentiometric study on PSS/C_{12}TAB.[15]

Poly(vinylsulfonate), PVS, has the same backbone structure and anionic sulfonate groups as PSS, but the polymer does not contain the hydrophobic phenyl group which PSS bears. Figure 5 shows the dependence of surface tension of 1.0 mM PVS solutions as functions of log [C_nTAB] in salt–free solutions. This Figure is in sharp contrast to the case of PSS solutions (Figure 1b): the quantitative and highly cooperative binding exhibited in PSS was not shown in PVS solutions. Though PVS/C_nTAB systems also showed the biphasic binding behavior similar to that in PSS/C_nTAB systems at high NaCl concentrations, the cooperativeness of binding was appeared to be much less even in the absence of NaCl. This clearly indicates that the high cooperative binding of surfactant cations on PSS results from the presence of the hydrophobic phenyl groups in PSS molecules. The hydrophobic interaction between PSS and surfactant molecules contributes to a great extent on the strength and cooperativity of the binding. From the dependence of the surfactant binding behaviors of PSS on the concentration of NaCl, it was also suggested that the electrostatic interactions between the surfactant cations and PSS is not negligible with respect to the hydrophobic interaction.

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Synthesis and Properties of Dicyclohexyltin(IV) Complexes. Structure of Cy₂Sn(S₂CNMe₂)₂

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Dicyclohexyltin(IV) complexes Cy_2SnX (X = O, S, $(Me_2NCS_2)_2$) have been prepared and characterized by means of elemental analysis, cryoscopic data, and IR spectroscopy. X–ray structure determination for $Cy_2Sn(S_2CNMe_2)_2$ (monoclinic; P2/c; a = 8.992(1), b = 6.688(1), c = 19.453(2) Å, β = 96.556(7) ; R = 0.041) has shown that the molecule is C_2-symmetric with both dithiocarbamate ligands bonding in anisobidentate mode and the local geometry around the hexacoordinate Sn(IV) atom is a distorted octahedral arrangement with the two cyclohexyl groups in trans position. The physical and chemical properties measured suggest polymeric and trimeric structures for Cy_2SnO and Cy_2SnS, respectively.

Introduction

Numerous dimethyltin(IV) and di–*t*–butyltin(IV) complexes have been investigated in order to understand the steric and inductive effects of organic ligands in their tin complexes. Physicochemical studies indicated that dimethyltin oxide is polymeric[1] while di–*t*–butyltin oxide is cyclotrimeric[2,3]. Dimethyltin sulfide has been found to be a 6–membered cyclic trimer[4,5] whereas di–*t*–butyltin sulfide is a 4–membered cyclic dimer[6]. Furthermore, X–ray crystallographic studies have shown that the coordination geometry of $Me_2Sn(S_2CNMe_2)_2$ is a distorted octahedral arrangement[7] in contrast to the distorted trigonal–bipyramidal structure of (*t*-

$Bu)_2Sn(S_2CNMe_2)_2$[8]. Thus it appears that there is a remarkable difference between $Me_2Sn(IV)$ and $(t-Bu)_2Sn(IV)$ complexes in chemical behavior. However, dicyclohexyltin(IV) complexes, median in bulkiness and inductive effect between dimethyltin(IV) and di–*t*–butyltin(IV) complexes, are surprisingly less well evaluated than their dimethyltin(IV) and di–*t*–butyltin counter parts although a few cyclohexyltin(IV) complexes were recently reported by the authors[9]. In an effort to understand the behavior of dicyclohexyltin(IV) complexes, we have prepared Cy_2SnX (X = O, S, $(Me_2NCS_2)_2$) and discussed in terms of their physicochemical evidences together with the crystal structure of $Cy_2Sn(S_2CNMe_2)_2$.