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Meso-tetrakis (N-methylpyridinium-4-yl) porphyrin 존재 하에서 sodium n-dodecyl sulfate 용액 성질

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Solution properties of sodium n-dodecyl sulfate in the presence of meso-tetrakis (N-methylpyridinium-4-yl) porphyrin

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요 약. 양이온성 수용성 5, 10, 15, 20-tetrakis(N-methylpyridinium-4-yl) porphyrin (TMPyP)의 존재 하에서 음이온 계면 활성제인 sodium n-dodecyl sulfate 의 용액 특성을 전도도법, UV-vis 및 공명 빛 산란 (RLS) 분광학적 방법을 이용하여 포괄적으로 연구하였다. 그 결과에 따르면 TMPyP 농도의 증가로 SDS 용액의 임계 미셀 농도는 감소하였는데, SDS 미셀의 안정화는 미셀 표면에 존재하는 음전하의 중화 때문이다. SDS용액 내에는 자유 포르피린 단량체, 미셀에 속박된 포르피린 단량체 또는 응집체, 그리고 nonmicellar porphyrin/계면 활성제 응집체와 같은 세 종류의 TMPy종이 분명히 존재하였다. 우리의 연구 결과는 SDS가 TMPyP의 응집을 유도한다는 것을 나타내었다. 실제로 두 종류의 J-aggregations이 관찰되었는데, 하나는 미셀에 속박된 포르피린 단량체 또는 응집체였으며, 다른 하나는 nonmicellar porphyrin/계면 활성제 응집체이다. 그러나, cmc이하에서는 TMPyP가 SDS 음이온과 정전기 상호작용을 나타내었다.

주제어: meso-tetrakis (N-methylpyridinium-4-yl) porphyrin, 계면 활성제, 응집, 공명 빛 산란

ABSTRACT. The solution properties of sodium n-dodecyl sulfate, as an anionic surfactant in the presence of a cationic water-soluble 5, 10, 15, 20-tetrakis (N-methylpyridinium-4-yl) porphyrin (TMPyP) has been comprehensively studied by means of conductometry, UV-vis and resonance light scattering (RLS) spectroscopies. The results represent the decreasing of critical micelle concentration of SDS solution due to increasing of TMPyP concentration. The stabilization of SDS micelle is due to neutralization of negative charge at the micelle surface. The presence of three different species of TMPyP in SDS solution has been unequivocally demonstrated: free porphyrin monomers, porphyrin monomers or aggregates bound to the micelles, and nonmicellar porphyrin/surfactant aggregates. Our results show SDS induced an aggregation in TMPyP. In fact two kinds of J-aggregations were observed: one of them for porphyrin monomers or aggregates bound to the micelles and the other for nonmicellar porphyrin/surfactant aggregates. However, the results represent the electrostatic interaction of TMPyP with SDS anion below the cmc.

Keywords: meso-tetrakis (N-methylpyridinium-4-yl) porphyrin, surfactant, aggregation, resonance light scattering

INTRODUCTION

Porphyrins play an important role in many biological processes, such as substrate oxidation reactions, oxygen transport and photosynthesis. The aggregation of porphyrin and metalloporphyrin provides insightful information in understanding the fundamental processes of living organisms and has been extensively studied in order to explain the biosynthetic formation and biological activity of naturally occurring compounds.[1] Under appropriate conditions with controlled ionic strength and protonation, porphyrins form highly ordered aggregates, namely J- or H-aggregates. J-aggregate is side-by-side arrangement of the porphyrin rings with absorption band red-shift, while H-aggregate is face-to-face arrangement of the porphyrins with absorption band blue-shift compared with porphyrin monomer. In the aggregation complex, the adjacent porphyrin molecules interact by hydrophobic interaction

or electrostatic attraction.[2,3] Anionic porphyrins have been known to aggregate spontaneously in water. It has been reported that tetrakis (4-sulphonatophenyl)-porphine ($H_2TPPS_4^{-2}$) and tetraphenylporphyrin trisulfonate ($H_2TPPS_3^{-}$) can form J-aggregates in aqueous solution with a high concentration of porphyrin or with high ionic strength.[4,5] Tetrakis (4-carboxylate phenyl)-porphine dication (TCPP) can also form J-aggregates in aqueous solution.[5-7] In contrast to anionic porphyrins, it was hard for cationic porphyrins to aggregate, especially for the meso-substituted cationic porphyrins, because the positive charges of the peripheral pyridinium groups are repulsive to each other.[8-11]

Binding porphyrins to the simplest models for membranes (surfactants micelles) has attracted much interest due to the possibility of understanding these biological processes. The issue of interaction with surfactants and monomer-aggregate equilibrium of porphyrin derivatives in micellar systems has also been reported.[12-23] In most cases, the interactions lead to the formation of porphyrin aggregates and/or micelle-encapsulated monomers with the exception of those porphyrin-surfactant pairs in which the interaction is electrostatic repulsive.[19] The structural, kinetic and spectroscopic studies on J- and H-aggregates can provide useful information for understanding molecular interaction in aggregation processes and for application of these materials in molecular devices and other applications. Different kinds of water-soluble porphyrins have various interaction styles with surfactants. In the presence of ionic surfactants below their critical micelle concentration (cmc), the free base porphyrins form aggregates,[24] whereas above their cmc, micellized monomer of porphyrin derivatives will be formed. It has been found recently that the formation of J-aggregate of anionic tetra sulphonated porphyrin was faster and more efficient in the presence of cationic surfactants, and the aggregation type can be controlled by varying the surfactant concentration.[25] Anionic porphyrins are micellized and exist as monomers in both cationic (cetyltrimethylammonium bromide (CTAB)) and neutral micelles (TX-100), but are present as aggregates in the anionic micelle (sodium dodecyl sulfate (SDS)),[26] however, cationic porphyrins only interact with anionic surfactant, and not with cationic CTAB and neutral TX-100 micelles.[27]

In this paper, the solution properties of tetra-cationic meso-tetrakis (4-trimethylaminophenyl) porphyrin (TMPyP) with anionic surfactant SDS was investigated by using room temperature coductometry, UV-vis and RLS spectroscopies. The variation of cmc of SDS in the presence of TMPyP and the aggregation behavior of TMPyP in the presence of various amounts of SDS were comprehensively investigated and interpreted on basis of intermolecular interactions.

EXPERIMENTAL

Materials

Meso-tetrakis (N-methylpyridinium-4-yl)porphyrin (TMPyP) was prepared according to the procedures described in literature.[28] Sodium dodecyl sulfate, was purchased from chemical reagents company of Merck which was used directly without further purification. All aqueous solutions were prepared by using twice distilled water. All of the measurements were done in 50 mM phosphate buffer, pH 7.0.

Apparatus

For the pHmetric measurement, we used a potentiometer (Metrohm model, 744). For conductometric measurements, an Orion 180 conductometer with a Radiometer conductivity cell was used. The absorbance measurements were carried out using UV-vis, Carry-500 double beam spectrophotometer with thermostat cell compartment. The light scattering measurements were done on a Shimadzu model RF-5000 spectrofluorimeter.

Methods

Conductometry: Solutions were kept at 25±0.1 ºC using a thermostated cell. Conductivity cell was calibrated by triplicate the conductivity of KCl solutions at different concentrations.[28] Experiments were carried out by adding different amounts of a stock surfactant solution to determine volume of buffer and measure the conductivity. The range of concentrations measured for surfactant varies in order to obtain enough points before and after the change of slope in the conductivity-surfactant concentration plots.

UV-vis Absorption Spectra

Aqueous solution of TMPyP (1.67×10^{-6} M) was titrated by adding appropriate volume concentrated solutions of SDS. The spectra were recorded after 3 minutes from the addition of SDS for ensuring the achievement of equilibrium.

Resonanse Light Scattering

The scattered-light intensity was monitored using the right-angle in the synchronous scanning regime of the excitation and emission monochromators in the region from 300 to 550 nm. The experimental light-scattering

spectra were corrected, taking into account the solution optical absorption and instrument sensitivity dependence on the wavelength as described in the literature. All experimental data are the averaged values of at least five independent experiments. The excitation and emission band pass were set at 3 and 5 nm, respectively. Aqueous solution of TMPyP (1.67×10^{-6} M) was titrated by adding appropriate volume concentrated solutions of SDS.

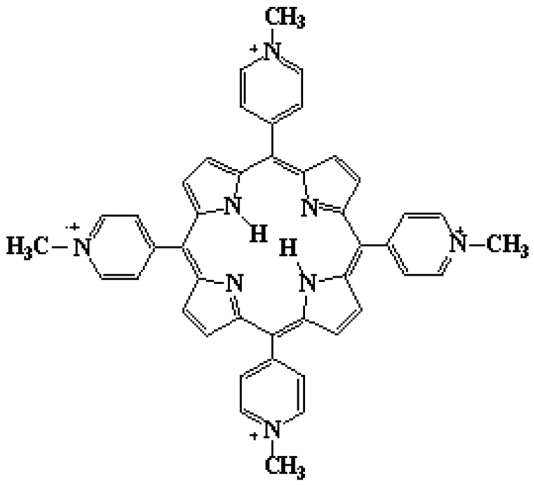
RESULT

Conductometry

The chemical structure of TMPyP is shown in *Scheme* 1, which is soluble in water. Deviation from the Lambert-Beer linear relationship of TMPyP occurred between 2.38-13.79 μM in water. The concentration of TMPyP used in this work was 1.67×10^{-6} mol/dm^3.

Conductometric titration provides an easy and fast way to calculate cmc values. When the conductivity of solutions with increasing concentration of surfactant is measured, the specific conductivity-surfactant concentration plots show two straight lines with different slopes. The first one corresponds to the concentration range below the cmc, when only monomers of surfactant exist in solution. At higher concentrations of surfactant, micelles start to form and a change of slope appears because the conductivity increases in a different manner. The intersection of these two straight lines is taken as the cmc value of the surfactant. A representative plot of conductivity versus total concentration of SDS is shown in *Fig*. 1. The cmc values at various concentration of TMPyP are shown in *Table* 1.

The results represent the decreasing of cmc values of SDS with increasing of TMPyP concentration. This represents the favoring role of TMPyP in micelle formation process. The stabilization of micelle by TMPyP can be due to neutralization of negative charge density of SDS micelle core or increasing of hydrophobic interaction of SDS tails due to solubilization of TMPyP in micelle core. The variation trend of conductivity of very low concentration of SDS represents the binding of SDS anion to TMPyP cation.



***Scheme* 1.** The chemical structure of TMPyP.

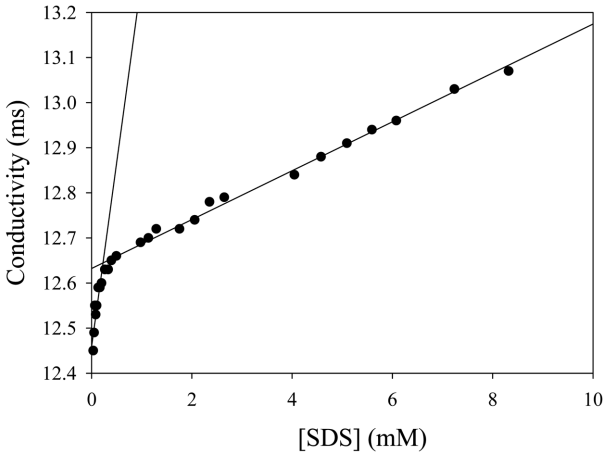


***Fig*. 1.** The variation of specific conductivity versus total concentration, of SDS in the presence of TMPyP (1.67×10^{-6} M). The value of cmc was estimated from the intercept values of two straight lines.

***Table* 1.** The calculation of cmc values of SDS in the presence of various amounts of TMPyP

TMPyP(M)	0.00	1.67×10^{-7}	5.72×10^{-7}	1.67×10^{-6}
cmc (mM)	1.27	1.10	0.87	0.18

Optical Absorption Measurements

The UV-vis absorption spectra of TMPyP in aqueous solution in the presence and absence of SDS are displayed in *Fig*. 2. It is observed that the addition of SDS changes the position, width, and intensity of the absorption spectra of TMPyP at different ratio of R=[SDS]/[TMPyP]. When the concentration of SDS was eight times of TMPyP concentration, the absorption spectra of TMPyP suddenly red-shifted from 426 nm to 434 nm and absorbance value leveled off. A well-defined isosbestic points at 398 and 451 nm were appeared, indicating that 1:8 TMPyP/SDS complex formed and the J-aggregates of the premicellar porphyrin-to-surfactant were induced, too. At further higher concentration of SDS above cmc, peak position of Soret-band returned to 431 nm, suggesting that J-aggregates of TMPyP/SDS complex decomposed gradually in favor of porphyrin monomers with the micelle.

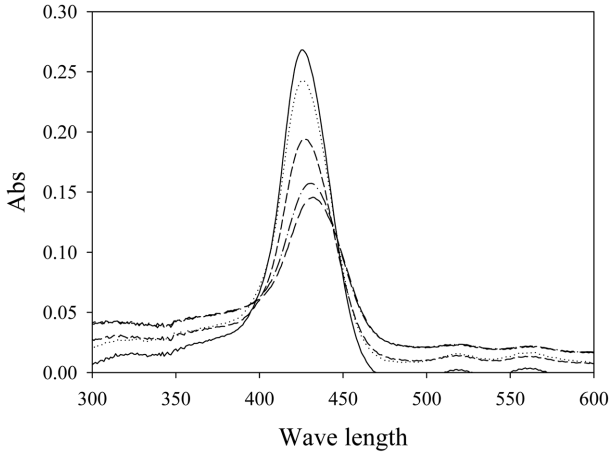


***Fig*. 2.** The UV-vis absorption spectra of TMPyP (1.67×10^{-6} M) in aqueous solution in the presence and absence of SDS (a) 0, (b) 0.14, (c) 0.26, (d) 0.38 and (e) 0.51 mM. The concentration of SDS is increased in the direction of arrow.

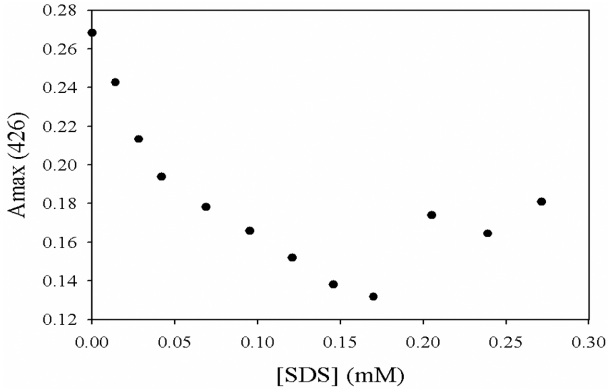


***Fig*. 3.** The variation of absorbance of TMPyP (1.67×10^{-6} M) at 426 nm versus total concentration of SDS.

The presence of isosbestic points are started from R=8 and ended in R=110 (cmc point) that is shown in *Fig*. 2. The small value in red-shifted wavelength of micellized porphyrin compared to that of free monomer indicated that TMPyP monomers were not encapsulated within apolar regions of SDS micelles but bound onto the surface of the SDS micelles by electrostatic interaction between the cationic groups of TMPyP and anionic surface of SDS micelles.

The most obvious change occurs in the Soret band region of the absorption spectrum, and an isosbestic points is observed, which indicates the presence of two type of TMPyP-SDS complexes in equilibrium with TMPyP monomer. The variation of absorbance at wavelength of Soret band (426 nm) versus total concentration of SDS is shown in *Fig*. 3. A big jump is observed at R value equal to 110, or at cmc point. The undefined trend that was observed after cmc point can be related to the formation of non-micellar porphyrin/surfactant aggregates.

Resonance Light Scattering

The scattered light intensity (SLI) of a solution in the absence of optical absorption depends on the wavelength as $1/\lambda^4$ (Rayleigh law). The buffer and surfactant solutions in the absence of porphyrin did not have absorbance band in the spectral range studied: thus, scattered light (SL) spectra of the solutions at different surfactant concentrations obeyed the Rayleigh law. The SLI slightly increases with the addition of surfactant. In the spectral range where a solution has optical absorption, an increased SLI can be observed as a result of the increase in the refractive index of the scattering medium in this range (resonance light-scattering (RLS) effect) (see Refs.[29,30] and references there in). The RLS spectrum of porphyrin solution should be from the free monomer, the J-aggregates, and out-micellized monomer. The RLS intensity of the monomer showed an obvious small intensity, while the aggregates showed high scattering intensity, illustrating that the size of the aggregates is large enough to scatter the light and the J-aggregates were multiple porphyrin units. *Fig*. 4 demonstrates the SL spectra of TMPyP (1.67×10^{-6} M) solutions in the presence of different SDS concentrations at pH 7. The SLI in the region of 300-550 nm at first increases dramatically due to the SDS addition (the RLS effect) and then decreases upon further increase in [SDS] and after cmc point with increase [SDS], the RLS effect was increased again. Our results indicated that the J-aggregates of the premicellar porphyrin-to-surfactant were induced when the 1:8 TMPyP/SDS complexes formed.

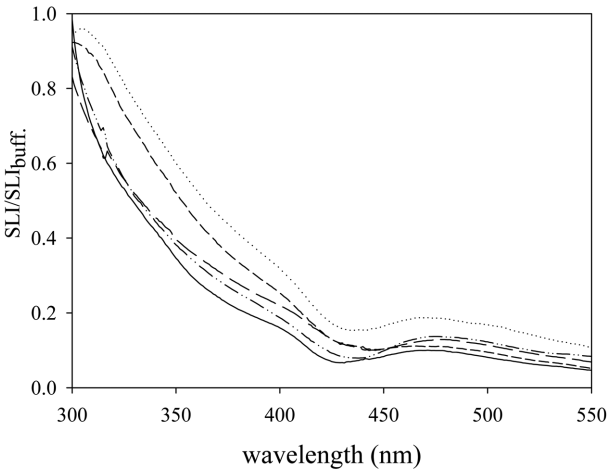


***Fig*. 4.** The RLS spectrum of TMPyP (1.67×10^{-6} M) in aqueous solution in the presence and absence of SDS (a) 0, (b) 0.14, (c) 0.26, (d) 0.38 and (e) 0.51 mM.

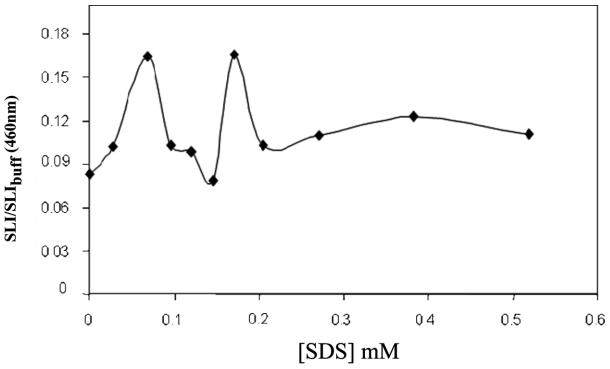


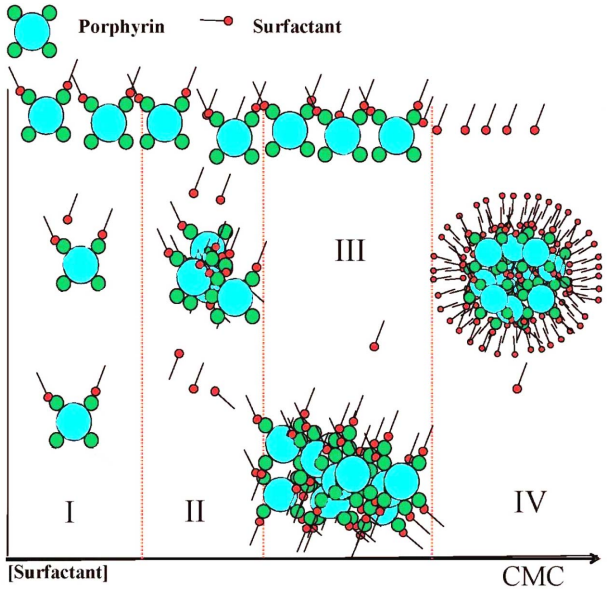
***Fig*. 5.** The intensity of the resonance light scattering of TMPyP solution (1.67×10^{-6} M) at λ=460 nm as a function of [SDS].

The SLI at 460 nm as a function of [SDS] is shown in *Fig*. 5. It confirms the above results with another shape. The maximum decrease in SLI is observed at [SDS]/[TMPyP] =110. This point is cmc that was obvious in conductivity and UV-visible absorption measurements. Hence, we can ascribe this bound species I to aggregates of TMPyP which are formed during the porphyrin binding to SDS at low concentrations of SDS and then after cmc point. Upon further increase of [SDS] the aggregates decompose in favor of the bound species II (which could be porphyrin bound monomers, dimers or aggregates). In the other hand when the concentration of SDS reached above cmc of about 1.46×10^{-4} M, the intensity of RLS decreased sharply to much a lower scale, indicating that the out-micellized monomer of TMPyP has been formed.

SUMMERY AND DICUSSION

The present study deals with the aggregation behavior of TMPyP in aqueous solutions in the present of different concentrations of SDS as surfactant. Various experimental methods were used for probing the different aspects of the SDS-TMPyP interactions. It was established that different phenomena occur, depending on the surfactant concentration, and these are qualitatively illustrated in *Scheme* 2.

At very low SDS concentrations (region I), the TMPyP-SDS solutions are characterized by UV-Vis and RLS. From the insignificant changes in light scattering and UV-vis spectra of these solutions, as compared to TMPyP solutions devoid of SDS, it can be concluded that almost no aggregation occurs in this region. However, after further increase of SDS concentration (region II), light scattering measurements indicate the formation of bulk colloidal particles. This technique indicates that positively charged particles are formed and these lead to increased scattering



***Scheme* 2.** The steps of interaction between TMPyP and SDS.

intensities which are 2-3 orders higher than those observed for porphyin solutions or for solutions of surfactant in lower concentrations. The decrease of dissolved porphyrin concentration is evidenced by the gradual decrease of the Soret band intensity, while the transformations occurring in the Q-bands seem to indicate that the two species (porphyrin and surfactant) have interacted. Since the RLS measurements in this SDS concentration region (II) show that the scattering intensity gradually increases as the concentration of SDS increases, it can be deduced that either the particle size or concentration increases. In fact in the presence of low concentrations of ionic surfactants with oppositely charges to the porphyrin, premicellar (or non-micellar) porphyrin-surfactant aggregates can be formed. This finally leads to massive aggregation and precipitation (TMPyP-SDS complex) (region III). This is in agreement with the results obtained by RLS, according to formation of bulk of Porphyrin and surfactant the scattering intensity gradually decreases as the concentration of SDS increases, it can be deduced that the particle size. This behavior continued until cmc point. After cmc point the excess of surfactant cause to increase the scattering intensity again because the negative charge increased around the bulk. Upon further increase of [SDS] the aggregates decompose in favor of the bound species II (which could be porphyrin bound monomers, dimers or aggregates).The presence of isobestic points in Uv-vis are started from R=8 (step II) and ended in R=110 ((cmc point) step (IV)) that is shown in *Fig*. 2. The small value in

***Table* 2.** The estimated cmc values of SDS in the presence of 1.67×10^{-6} M TMPyP by different methods

methods	cmc
conductometry	0.18
UV-vis	0.17
RLS	0.15

red-shifted wavelength of micellized porphyrin compared to that of free monomer indicated that TMPyP monomers were not encapsulated within a polar regions of SDS micelles but bound onto the surface of the SDS micelles by electrostatic interaction between the cationic groups of TMPyP and anionic surface of SDS micelles. The experimentations also show that SDS induced an aggregation in TMPyP. In fact two kinds of J-aggregations were observed, one of them for porphyrin monomers or aggregates bound to the micelles and the other for nonmicellar porphyrin/surfactant aggregates.

In the case of the TMPyP-SDS system and in SDS concentrations below the cmc (region IV), the Soret band is red-shifted compared to that of the porphyrin. Unlike the porphyin, the Soret peak of the porphyrin-SDS solutions in region IV is asymmetric. This seems to imply that there is a dispersion of particles with different size and structure in these solutions and that the peak of the Soret band is a superposition of their light absorption properties.

Also the above experimentation indicates that the cmc of the SDS in the present of TMPyP can be obtained via conductometry, UV-Vis, and RLS (*Table* 2). The reducing of cmc in the presence of TMPyP can be related to stabilization of SDS micelle due to neutralization of negative charge at the surface of micelle.

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