[Review]

^1H NMR Studies of Surfactants in Aqueous Solutions*

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Abstract Surfactant is a substance that lowers the surface tension of the medium in which it is dissolved. They form oriented colloidal aggregates, micelles, when a specific concentration is exceeded and abrupt changes in physical properties of the solution will be observed. Surfactant systems have been proved to be very useful in many biological and industrial processes. Properties of these systems have been intensively investigated by many spectroscopy methods, especially proton nuclear magnetic resonance (^1H NMR). It has played more and more important role in the continued development of NMR new techniques. Characterization of micellization processes, physical properties of micelles, e. g. structure, size and shape, hydration of micelles, solubilization by micelles, interaction between micelles of different kinds of surfactants, and that with biological compounds and with polymers were studied by the existing sophisticated NMR techniques. These investigations demonstrate that NMR spectroscopy is a versatile technique for the study of surfactants. It provides information at a molecular level that is not available by other spectroscopic methods. Chemical shift changes, relaxation experiments and NMR self-diffusion measurements are almost used routinely. The use of two-dimensional NMR spectroscopy, 2D NOESY and HOESY is a growing trend in studying the chain packing in micelles as well as interactions between micelles with other molecules, biological and polymeric. These methods provide a deeper insight into the relative arrangement of surfactant molecules in an associated assembly.

Keywords: NMR, Relaxation, Self-diffusion, Surfactant, Chemical shift

Surfactants are molecules with two distinctively different parts: hydrophobic and hydrophilic groups. This is known as an amphipathic structure. They lower the surface or interfacial tension of the medium in which they are dissolved. The abrupt change in physicochemical properties seen in aqueous solutions of surfactants when a well-defined concentration is exceeded is attributed to the formation of oriented colloidal aggregates, micelles. The narrow concentration range over which these changes occur has been called the critical micelle concentration (cmc).

Ever Since McBain^[1] proposed the presence of molecular aggregates in soap solutions, the structure of micellar aggregates has been a matter of discussion^[2]. The details of micellar and mixed micellar structures have been intensively investigated over the years and almost every technique devised by modern science, such as X-ray diffraction(XRD), nuclear magnetic

resonance(NMR), electron spin resonance (ESR), small-angle neutron scattering(SANS), light scattering, fluorescence, calorimetry, chemical relaxation, ultrasonic relaxation and spectroscopic techniques, have been applied^[3-5]. Nuclear magnetic resonance has played more and more important role in the continued development of NMR new techniques in the studies of micelles, especially at the end of last century. Several reviews have appeared on the subject^[6-11]. Among the nuclei accessible in NMR studies ^1H is most useful because of its high natural abundance and sensitivity^[6-11]. The present contribution will be concerned with the characterization of micellization processes physical properties of micelles, the structure of self-aggregated micelles, hydration and solubilization properties, interaction between micelles of different kinds of surfactants and polymers by the existing ^1H NMR techniques at a molecular level. It is sure that to monitor chemical shift changes as a function of the

surfactant concentration would be the simplest approach based on NMR. However, there are many other NMR sophisticated experimental methods conveniently available nowadays which can provide abundant information about the structure and dynamics of micelles, interaction between surfactants, and between surfactant and polymers in their co-aggregates. These methods are NMR relaxation, self-diffusion coefficient, and especially the multi-dimensional NMR measurements developed for the structural determination of complex organic compounds, and biological macromolecules, such as, proteins and nucleic acids. The 2D NOESY and 2D HOESY appeared to be effective tools to elucidate the interaction between surfactant molecules of one kind or of different kinds, between water molecules and surfactants and between surfactant and polymer molecules. It is worth to emphasize that it is often difficult to make confirmative conclusion from the observed NMR data by the use of a single NMR method at a time. Combination of several NMR methods is sometimes necessary. We do not attempt to cover all of the existing works, but a number of studies will be selected, to show which NMR methods, except widely used chemical shift changes are suitable to solve a given problem of interest.

1 NMR relaxation

Besides the chemical shift and band shape NMR parameters, spin-lattice relaxation measurement is another approach for monitoring the micellization process. The spin-lattice relaxation time of a nucleus is affected by its local dynamics. Therefore, the spectral data may vary as a function of the concentration of the surfactant and should exhibit an inflection point when the micelles are formed, because the self-aggregation of the surfactant molecules induces a change in the chemical environment as well as the freedom of the motion of the surfactant molecules. For several surfactants the change in ^1H chemical shifts with surfactant concentration is very slight and hardly shows any significant inflection point that can be an indication of a micellization process, such as sodium cholate. However, the spin-lattice relaxation time (T_1) of sodium cholate varies with its concentration. At the cmc, the molecular correlation time increases substantially since they change from molecularly dispersed to self-associated form. A sharp decrease in T_1 at $16.0 \text{ mmol} \cdot \text{L}^{-1}$ was found which is close to the cmc value obtained by fluorescence method^[12]. Variation of the spin-lattice and spin-spin relaxation times (T_1 and T_2) as a function of the surfactant concentration was also demonstrated for the well known ionic and non-ionic surfactants, sodium dodecyl sulfonate, cetyl tri-methyl ammonium bromide and Triton X-100 (*p*-tert-octyl phenoxy- polyethoxy-ethanol). It was shown that the ratio of T_2/T_1 , which gives a measure of the degree of departure of the

molecular motion from the extreme narrowing condition, gives sharper turning points on the concentration dependence curve than that of the chemical shift one^[13]. Microstructure of surfactant micelles has been studied early in the sixties of the last century by ^1H spin-lattice relaxation times of hydrocarbon chain protons in solution of sodium alkyl sulfates. The results indicate that when micelles are formed the relaxation rate of the CH_2 protons is remarkably increased as their environment changes from D_2O to liquid hydrocarbon. The relaxation rate of CH_2 protons in micelles suggests that part of the alkyl chains in the micelles are exposed to water, and that molecular motion in the micellar interior is more restricted than in a liquid hydrocarbon of the same chain length as the single ions making up the micelles. While the rotational and internal motions of alkyl chain compounds are much the same in aqueous as in non-aqueous solvents, but the translational motion is more restricted in aqueous solvent^[14]. For the non-ionic surfactant, *p*-tert-octyl phenoxy(polyethoxy) $_n$ ethanols, where $n=9 \sim 10$, $12 \sim 13$, and 30 , spin-lattice relaxation measurements of the protons reveal that the micelle interior is liquid like and is not penetrated by solvent to any significant extent. The internal methyl and methylene groups of the hydrocarbon chain are actually in a more non-polar environment in the micelle than in the bulk detergent. Contact with solvent seems to begin in the region of the first ethoxy group following the phenyl group and gradually increases toward the other end of the chain. The mobility of the segments increases in the same direction. Water molecules in the region between the polyethoxy chains appear to be partially immobilized^[15]. Simulation of the decay curves of ^1H NMR spin-spin relaxation of three types of surfactants (cationic, anionic, and non-ionic) in aqueous solutions shows that the protons of the methylene groups nearest to the polar heads relax bi-exponentially. The fast relaxing component is attributed to the part of segments of the hydrophobic chains, situated near or on the surface of the hydrophobic micellar core, while the slower relaxing component is attributed to the rest part staying in the interior of the micellar core. The faster the protons relax and the larger this component, the more compact is the micellar core^[16]. Results show that the micellar core of sodium dodecyl sulfate is more compact than that of cetyl tri-methyl ammonium bromide. The bi-exponential behavior of the decay curve for the first oxyethylene oxide segment next to the phenoxy ring of Triton X-100 suggests that this oxyethylene groups participate in the formation of the surface layer of the micellar core^[16]. Solvent spin-spin relaxation measurements indicates that the ethylene oxide segments in the adsorbed layers of C_{12}E_6 and $\text{C}_{12}\text{E}_{25}$ on hydrophilic surfaces have more conformational restrictions than those in polyethylene oxide layers because of the association of

the aliphatic tails^[17]. The NMR paramagnetic relaxation method using the 3-carboxy propyl anion as the relaxation agent for anionic micelles has been developed as an alternative procedure for the determination of distribution coefficients of solubilizates in micellar systems^[18], solubilization equilibria for anionic micelles^[19], and solubilization and aggregation numbers in micellar mixtures of anionic and cationic surfactants with solubilized tetraethylene glycol and tetraethylene glycol dimethyl ether^[20].

2 Self-diffusion coefficient

The NMR self-diffusion coefficient measurements provide a convenient tool for the study of micellization process. It is based on the large intrinsic difference in self-diffusion rates for monomeric and micellized surfactant molecules. The monomer lifetime in a typical micelle is short on the time scale of the self-diffusion measurement, so all the self-diffusion coefficients will become time averaged. Thus the observed self-diffusion coefficient can be expressed analogously to the case of chemical shift. The cmc measured ($2.6 \text{ mmol} \cdot \text{L}^{-1}$) for the aggregation of sodium di-2-ethyl hexyl sulfosuccinate (Aerosol OT) is in good agreement with that measured by surface tension method^[21]. The NMR self-diffusion coefficient measurement method was widely used to measure the cmc of various surfactants. It is an important method to estimate the size and shape of the micelles formed. It gives direct and easy interpretable information. From the translational self-diffusion coefficient of the micelle one can deduce the hydrodynamic radius using the Stokes-Einstein equation. It should be noted that in estimating the hydrodynamic radii the effect of inter-micellar interactions must be taken into account. A series of researches on the size of micelles formed in aqueous solutions of non-ionic amphiphiles, polyethylene glycol alkyl ethers (CxEy), were performed by using NMR self-diffusion coefficient measurements. A coherent picture of micelle size of C_{12}E_6 as a function of temperature was obtained^[22]. The errors caused by convection in variation in temperature during measurement of a member of the oligooxylene alkyl ether groups, C_{12}E_6 , make the determined results less precise than those obtained by other methods^[23]. Normally micelles are spherical with a radius equal to the length of the extended surfactant molecule. When the size of the micelles grows beyond this limit it may cause a change of their shapes. Self-diffusion coefficient measurement with the consideration of obstructing effect may be an approach to solve this problem^[24-25]. Self-diffusion coefficient measurement of the surfactant molecules and water protons suggests that dodecyl tri-butyl ammonium bromide micelles are spherical at a concentration range of 0 ~ 80% volume fraction^[26]. Mixed micelles of non-ionic (C_{12}E_5 , C_{12}E_8) / anionic (sodium dodecyl sulfate) and cationic (dodecyl tri-methyl ammonium chloride) surfactants were studied by self-diffusion coefficient already in the eighties

of last century^[27-28]. Results show good correlation between the self-diffusion coefficient and the line width measurements. A minimum on the self-diffusion coefficient *vs* mole fraction of C_{12}E_5 curve occurs at the concentration of 20% of sodium dodecyl sulfate, after that the self-diffusion coefficient increases. The appearance of the minimum was attributed to the repulsion between micelles and the increase in self-diffusion coefficient to a decrease in micellar size. The observed decrease in self-diffusion coefficient as one starts to replace the non-ionic by ionic is mainly due to an increase in micelle-micelle repulsion. Then a diffusion mechanism in which monomers can be exchanged between different aggregates is partly inhibited. The increase in self-diffusion coefficient occurring at higher fractions of ionic surfactant is shown to be due to a decrease in micellar size. Small additions of ionic surfactant dramatically increase the cloud point temperature, but negligibly affect the observed self-diffusion coefficient^[27].

3 Multi-dimensional NMR spectroscopy

It is well known, that the two-dimensional nuclear Overhauser enhancement spectroscopy (2D NOESY) is an effective method to study the three-dimensional structure of large molecules, such as proteins, which have long motional correlation time of molecule^[29,30]. Cross dipolar interaction peaks in a NOESY spectrum rely on the cross relaxation of longitudinal magnetization during the mixing time. One can extract valuable information about inter-molecular distances from the intensity of the NOESY cross peaks. The appearance of cross peaks between protons attached to remote methylene carbon atoms of the surfactant molecules in a 2D NOESY map can be an indication of micellization, because cross peaks appears in the 2D NOESY map only from proton pairs separated less than 0.5 nm apart in space. While the distance between protons attached on remote carbon atoms on a hydrocarbon chain is far longer than this value. The 2D NOESY map of a dilute (0.5 cmc) triton X-100 aqueous solution shows only cross peaks between protons attached to the adjacent carbon atoms in the hydrocarbon chains. While cross peaks between protons of the remote methylene groups exist in the 2D NOESY map of concentrated (10 cmc) Triton X-100 aqueous solution^[31]. A conformational change of the alkyl chain of sodium cis-7-dodecenyl sulfate was observed upon micellization through the appearance of dipolar interaction between remote protons^[32].

Distances between proton pairs of Triton X-100 in the aqueous solution below and above its cmc were calculated according to the intensity dependence on the $1/r^6$ power of the distance between the proton pairs, r^6 . By comparing with the theoretical results calculated by HYPERCHEM, it was shown that the hydrophilic polyoxyethylene chains in the molecular

dispersed state are extended, while in self-aggregation they become coiled, forming a layer thick in dimension and loose in structure surrounding the hydrophobic micellar core with a certain number of water molecules included^[31]. Care should be taken in this experiment that suitable mixing time should be selected so as spin-diffusion in the system was avoided to get accurate results of proton distances^[33]. Besides, the combination with NMR relaxation measurements indicates the participation of the first oxy-ethylene group, which is next to the phenyl group, in the formation of the rigid surface layer of the hydrophobic micellar core. The use of hetero-nuclear cross relaxation between water protons and nuclei of surfactant atoms seems to be promising^[34-38]. Average location of water with respect to octanoate and decanoate polar heads in micelle was obtained directly from hetero-nuclear cross polarization from water protons to non-protonated carbonyl nuclei of the surfactant. The water-surfactant polar head distance was found to be around 0.3 ~ 0.4 nm^[37]. Because of the large chemical shift dispersion range, 100% natural abundance, and the large magnetogyric ratio of ^{19}F , ^1H - ^{19}F cross relaxation studies between water protons and surfactant fluorines are potentially helpful in estimating hydration of amphiphile micelles. A small and positive cross-relaxation rate shows that the water residence time in the head group region of a fluoro-surfactant is short. The distance between water protons and the first CF_2 segment is small, indicating strong water penetration to the depth of the first segment of the alkyl chain^[38].

The two-dimensional NOE spectroscopy (2D NOESY) technique was found to provide deeper insight in terms of the solubilization of molecules in the interior of micelles. Significant positive cross peaks between protons of the sodium dodecyl sulfate micelle and those of the solubilizates (1-butanol and benzene) as well as between protons of benzene and dodecyl trimethyl ammonium bromide micelle protons were observed in the 2D NOESY map. This correlates well with the expected results^[39].

2D NOESY experiments of mixed surfactant system (CTAB/Triton X-100) give direct information about the interactions among the molecules of the two surfactants inside the mixed molecules. Comparing with the inter-proton distances of these Triton X-100/cetyl tri-methyl ammonium bromide mixed micelles with those of the self-aggregated Triton X-100 micelles^[13] one can notice that in the mixed system Triton X-100 molecules are separated apart from each other as if they were in the single molecular state of dilute solution at a concentration below its cmc. It is worth to notice that the intensity of the cross peak between the hydrophobic and hydrophilic protons of Triton X-100 becomes weaker with the increase in the molar ratio of CTAB/Triton X-100. It suggests that the conformation of the

coiled long poly-oxyethylene chains of Triton X-100 micelles becomes extended as more and more CTAB molecules with large tri-methyl groups are inserted into the mixed micelle^[40]. Cross peaks between the hydrophobic protons of sodium dodecyl sulfate and those of Triton X-100 appeared in the 2D NOESY map of their mixed solution, suggesting that the hydrophobic chains of the two surfactants are in close proximity, i. e. they are mixed in the hydrophobic micellar core. In contrast to the case of the mixed micellization of Triton X-100 with cetyl trimethyl ammonium bromide, the intensities of the cross peaks between the hydrophilic and hydrophobic protons of Triton X-100 on the 2D NOESY map did not show any remarkable changes with the increase in the fraction of sodium dodecyl sulfate in the mixed solution. This suggests that the conformation of the hydrophilic chains of Triton X-100 remains coiled in mixing with sodium dodecyl sulfate, which has a smaller polar head than cetyl tri-methyl ammonium bromide^[41]. Similar steric-hindrance effect on the conformational change of the hydrophilic poly-oxyethylene chains of a non-ionic surfactant, Brij-35, having a longer hydrophilic chain than that of Triton X-100 was observed by mixing with the cationic surfactant, cetyl tri-methyl ammonium bromide, while mixing with sodium dodecyl sulfate does not show this effect^[42]. 2D NOESY experiment of a solution of sodium dodecyl sulfate at a concentration of about twice the cmc and $2\text{ g} \cdot \text{L}^{-1}$ of polyethylene oxide showed that the polymer penetrates into the surfactant micelles^[43]. There is no cross relaxation peaks between the protons of the surfactant and the polymer at concentrations between the so called cac and cmc, while cross relaxation peaks between surfactant remote protons do exist, suggesting the start of self-aggregation of sodium dodecyl sulfate molecules at cac. The appearance of strong cross peaks between the protons of the polymer and the protons of the methylene protons farther from the polar head groups of the surfactant support the conclusion that the polymer is solubilized in the interior of the surfactant micelles at the surfactant concentration above its cmc^[44].

Two-dimensional heteronuclear Overhauser enhancement experiment (2D HOESY) of the poly-acrylamide-Triton X-100 aqueous solution showed the absence of cross peaks between the protons of Triton X-100 and ^{13}C of poly-acrylamide. The presence of cross peaks among the protons of Triton X-100 molecules significantly implies that interaction among the protons of the surfactant molecules is far stronger than that between protons of the polymer and the surfactant. The appearance of cross correlation peaks between hydrophobic protons and hydrophilic carbon nuclei and *vice versa* of the same pairs of groups of Triton X-100 in the 2D HOESY map gives strong evidence for the coiled and folded feature of the loosely packed hydrophilic chain of Triton X-100 upon micellization in the

presence of the polymer in aqueous solution^[45].

4 Conclusion

NMR spectroscopy is a versatile technique for the study of micelles, elucidating the micellization process, the physical properties and structure of micelles, and interactions between micelles and various kinds of substances. Chemical shift changes, from which the cmc, aggregation number and counterion binding can be deduced, are easily followed thereby widely used. Relaxation experiments provide information about dynamic properties of the surfactant molecules involved in the micelles. Self-diffusion coefficient measurement is an important tool to get information about the size and shape of micelles. With the aid of phase separation model analysis composition of mixed micelles can be evaluated. The use of two-dimensional NMR spectroscopy, 2D NOESY and HOESY is a growing trend in studying the chain packing in micelles as well as interactions between micelles with other molecules. It provides a deeper insight into the relative arrangement of molecules in an associated assembly.

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表面活性剂在水溶液中性质的质子核磁共振研究*

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摘要 综述了质子核磁共振的几种方法在表面活性剂水溶液研究中的应用。自从上世纪六十年代以来的许多研究表明核磁共振的各种技术是研究表面活性剂溶液的有效手段。它可以提供表面活性剂在水溶液中的 cmc、胶束的结构、尺寸、水化、加溶性质和位置, 不同表面活性剂胶束之间的相互作用, 以及胶束与生物分子和高聚物的相互作用。化学位移已经成为惯常方法, 弛豫测量提供动态信息, 自扩散系数测量是研究胶束尺寸的很好手段。近来由于核磁共振技术的不断发展, 用于研究生物大分子的 2D NOESY 和 HOESY 也逐渐应用到研究表面活性剂聚集结构中。由此可以得到有关表面活性剂在水溶液中行为的分子水平信息, 是其它谱学方法所不能及的。

关键词: 核磁共振, 弛豫时间, 自扩散, 表面活性剂, 化学位移

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