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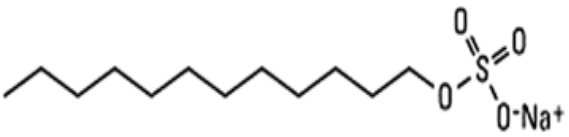
LIPID INDUCED MICROSTRUCTURAL TRANSITIONS IN AQUEOUS DISPERSIONS OF COMMON SURFACTANTS: MICELLE-VESICLE-MICELLE

Sachin Abhilash Chaturvedi, Dr. Mohammad Muzzamil Kuddushi
Organic Chemistry, Parul University
Vadodara, India

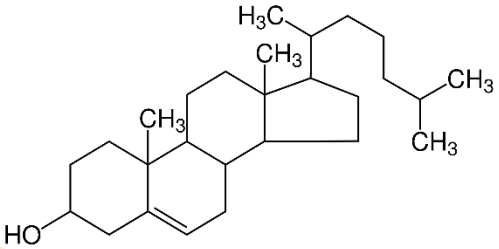
Abstract: A stable vesicle aggregation is a must for transporting and delivering biological and pharmacological standards. By happenstance, non-lipid vesicles made of non-lipid building blocks such common surfactants (CSs) were discovered and outperformed the competition. We examined lipid (cholesterol)-driven unilamellar vesicle formation in aqueous CSs in order to manufacture persistent, more stiff, and hydrophobic vesicles from standard surfactants. The vesicles have a high level of stability. The vesicles were studied using spectroscopic (turbidity measurements and fluorescence spectroscopy studies), scattering (dynamic light scattering), and transmission electron microscopy techniques. Using fluorescence techniques, the hydration behaviour and stiffness of the vesicular bilayer following conversion from micellar meeting were examined. The resulting unilamellar vesicles are compared to sodium dodecyl sulphate, a common surfactant.

I. INTRODUCTION

Micelles, vesicles, and lamellar phase are examples of organised aggregates formed by amphiphillic molecules in aqueous solution. The aggregate structure of numerous types of aggregates can be altered by using external variables[1]. Vesicles are chemical-storage and-transport capsules with a membrane covering[2].Cationic vesicle structures are simple to make, but correct conformational changes are necessary for specific functionalities to be achieved. There's a chance they'll be used as controlled drug delivery vehicles[3], model membranes[4], and microreactors[5]. Vesicles are closed bilayer globular forms that can be monolamellar or multilamellar. In the aqueous environment, they are amphiphilic molecules that are extensively utilised as cell membranes and transporters for hydrophilic or lipophilic chemicals. When it comes to molecular drugs, there are no exceptions [6-12]. Liposomes are phospholipid-derived vesicles that have been employed as drug delivery vehicles on numerous occasions[13-15]. It has been shown to be hydrolyzed and destroyed oxidatively [16,17]. The system's kinetic instability is exacerbated by the poor solubility of phospholipids in aqueous media [13]. To circumvent these problems, non-phospholipid amphiphiles such as common lipid amphiphiles have been utilised. Surfactants, block copolymers, polypeptides, Dendrimers, fullerene derivatives, and polysaccharide derivatives with amphiphilic side chains are all examples of constraints in drug delivery systems. The key grounds for their acceptance are the advantages of common surfactants over their conventional equivalents [18]. Micelles, for example, form at room temperature and have a low critical micellization concentration (cmc), high surface activity, and a low kraft temperature, as well as excellent surface wetting capability, detergency, and solubilization[19-21]. Incorporation of cholesterol(cho) produces stiffness in the vesicular bilayers, which stabilises the vesicular assembly. Ion and oxygen transport are improved by a factor of two when cholesterol is added. Cationic[23,24], anionic [25], and non-ionic compounds in aqueous surfactants [26,27] vesicle bilayer compression[22] cholesterol-induced vesicle formation cationic [23,24], anionic [25], and non-ionic compounds in aqueous surfactants.



Sodium Dodecyl Sulfate (SDS)
MW 288



Cholesterol (CHO)
M.W=386.65
Fig.1 structural representation of the sodium dodecyl sulfate and cholesterol

Individual ingredients of the mixture (cho and CSs) can generate vesicles in aqueous medium in the range of concentration studied. Cho is a hydrophobic molecule that is frequently employed as a hardener and stabiliser. Membranes, both natural and artificial, interact with one another to form crystals in water. More hydrophobic multilayer vesicles are produced when the CSs work together. Micelles Surfactants' increased vesicular system performance is critical in the development of more effective medicine delivery systems. Bottom-up methodologies for generating bespoke nanomaterials with fine size control are best demonstrated by these systems. Determine the mechanisms that underpin this synergistic interaction and the impact of new functionalities on the entire surfactant group in the development of tougher surfactants. Concentrate your efforts on molecular aggregates.

Keywords : Cho-Cholestrol, SDS-Sodium Dodecyl Sulfate

II. EXPERIMENTAL SECTION

MATERIALS AND METHODS

The common surfactant used in this present investigation (sodium dodecyl sulfate) $NaC_{12}H_{25}SO_4$ were found in our laboratory . the common surfactant were stored under reduced pressure prior to the measurements sodium dodecyl sulfate (>97%purity), SRL INDIA provided pyrene (>99 percent purity) which was used without additional purification. SRL INDIA provided me with cho (purity: 99%). Throughout the experiment, double distilled water deionized milli-q-water was employed.

STRATEGY FOR THE SOLUTION PREPARATION

To make vesicular aggregates, the requisite quantity of surfactant molecules $NaC_{12}H_{25}SO_4$ sodium dodecyl sulphate and cholesterol was weighed in sealed glass containers and placed in the double distilled water.Prior to the measurements, the resultant mixes were sonicated for 2 minutes (sonics vibracell) at 20 KHZ until homogeneous, and all of the solutions were stored at room temperature for 7 days to maintain thermodynamic equilibrium.

TURBIDITY MEASUREMENTS

Varian carry 50 spectrophotometer equipped with a thermostated cell compartment Throughout the research, it was used. A quartz cuvette with a 1 cm route length was employed. With increasing concentrations of cho, optical densities for cho/amphiphile mixtures (cho/sodium dodecyl sulphate) in aqueous solution were tested. The wavelength for measuring optical density was chosen to be 450 nm, where sodium dodecyl sulphate and cho had no absorption. Any variations in optical density are attributed to light scattering by bigger aggregates created by many molecules interacting with the amphiphile.

STEADY STATE FLUORESCENCE MEASUREMENT

Fluorescence spectrophotometer Cary eclipse (varian ltd,us) The steady-state fluorescence spectra were obtained using this method. With such a 5 nm excitation and emission slit width, the fluorescence intensity of pyrene, the polarity probes (3*10-6mM), was obtained from 350 and 500 nm for an excitation wavelength of 334 nm.

DYNAMIC LIGHT SCATTERING (DLS) MEASUREMENT

The DLS measurements were carried out at 298.15+- 0.1kelvin using zetasizer nano ZS90 (malvern,uk) in a disposable sizing cuvette.

TRANSMISSION ELECTRON MICROSCOPY (TEM)

At a voltage of 200 kilovolt, A JEOL model JEM 2010 transmission electron microscope (TEM) was used for transmission electron microscopy (TEM). With a staining agent of 0.5 wt % uranylacetate, TEM images of the vesicles were obtained.

RESULTS AND DISCUSSION

The hydroxyl group of cholesterol interacts synergistically with the head group of the common surfactant, and the hydrophobic component of cholesterol binds hydrophobically well with carbon chain length of the surfactant functioning inside the head group. At lower cholesterol concentrations, it increases interaction and leads to the formation of larger aggregates. The level of concentration of cholesterol in the micellar solution of CSs grows as the concentration of cholesterol in the micellar solution rises. bigger aggregates, most likely of mixed micelles, form. Vesicles form when the concentration of cholesterol reaches the threshold for creating mixed micelles, the amount at which cholesterol saturated mixed micelles, and vesicles break down and are converted back to micelles when the concentration of cholesterol is increased.The addition of a more hydrophobic head group causes the bilayer membrane to produce vesicles with increased stiffness and hydrophobicity. The morphological transition (micelles-vesicles-micelles) can be clearly seen by monitoring many physical characteristics is a function of the system increased cholesterol concentration. The toughness and hydrophobicity of such vesicular bilayers generated in cholesterol/surfactant systems may be investigated using spectroscopic probes.

We investigated how cholesterol levels affected a variety of system physical attributes in the current study.The surfactant's cmc is 8 mM for sodium dodecyl sulphate. We used an 80 mM surfactant solution, which suggests it's micellar in nature. Turbidity, DLS, and TEM were the methods we used.Turbidity is lower in smaller aggregates, but it grows as the micellar transition occurs from (micelles-vesicles-micelles). The aggregate size was determined using DLS measurements,

Transmission electron microscopy images were used to identify the exact form and size of the aggregates. The above-mentioned morphological alterations were caused by introducing cholesterol molecules into to the micellar solution.At lower cholesterol concentrations, SDS, a common surfactant, demonstrates micellar transition. It produces a stiffer and more hydrophobic bilayer than the other surfactants studied. Fluorescence methods were used to determine the bilayer membrane's hydrophobicity.

TURBIDITY MEASUREMENTS

The turbidity of the solution was evaluated at 298.15 kelvin to study the changes in the microstructural aggregates formed by the common surfactant sodium dodecyl sulphate $NaC_{12}H_{25}SO_4$ and cholesterol combination in aqueous solution. The optical density varies at 450 nm.

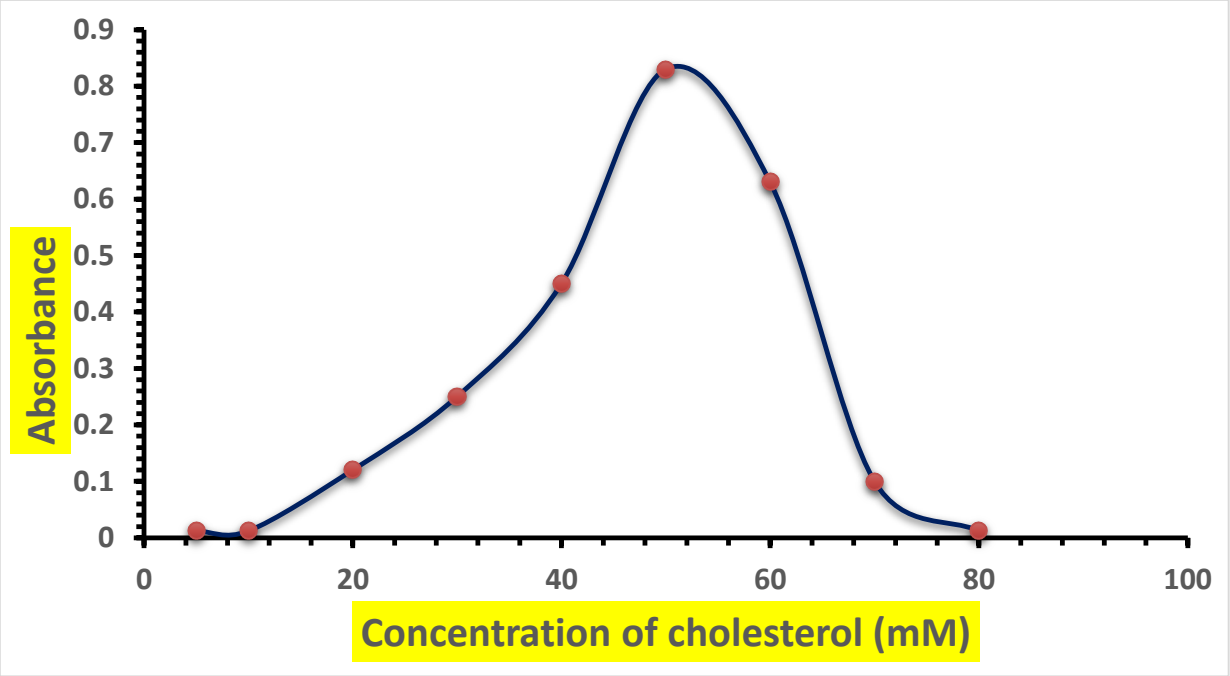


Fig.2 Standardized absorbance plot of $NaC_{12}H_{25}SO4$ (82Mm) aqueous solution in the presence of various cholesterol concentrations

At a fixed concentration of SDS (80mM), absorbance was found to be near nil with an increase in amounts of cholesterol at a minuscule concentration of (0.5mM), and samples appeared clear, most likely because of SDS's spherical aggregates sizes that are smaller[28] therefore, as cholesterol concentrations rise, optical density reaches a maximum and after that declines to a seeming a fixed value. Increased turbidity is also a factor indicates a larger aggregate size, implying a micellar transition[29,30].

In the current investigation, the concentration of cholesterol required to obtain the greatest optical density (50mM) demonstrated that common surfactants interacted strongly. The turbidity of the cholesterol dominating zone is greater than turbidity of the amphiphilles dominating geographical area in all of the studied systems. This happens because the aggregates during the latter phase are bigger than the neat amphiphiles. When cho concentration rises, turbidity rises as well. as demonstrated in the images in figure 4. All groups of solutions appeared transparent with lower cho concentrations. The clarity of the solutions improved As the amount of cho in the system grew, so did the amount of cho in the Solutions were milky white at first because there are huge scatters in the solution, most likely vesicles appeared at (50mM), and again increase the concentration at (70mM) the micelles again start forming, subsequently became colourless as concentration was increased. This is how the tyndall effect, which is caused by the presence of huge scatters in a solution, is expressed.

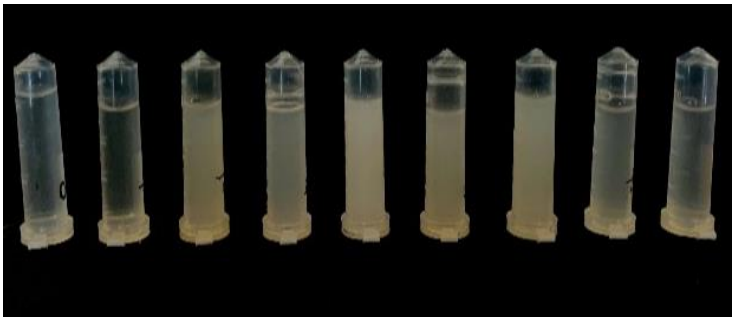


Fig.3 image of the cholesterol/$NaC_{12}H_{25}SO_4$ solution with increasing concentration of cholesterol in transparent bottles.

STEADY STATE FLUORESCENCE STUDIES

Employing steady state fluorescence spectroscopy, the rigidity or hydrophobicity of the vesicular assemblies generated by cholesterol/surfactant mixtures were investigated and compared.Pyrene, a fluorescent probe used to examine dipolarity inside organised media, was utilised in this study, and the ratio of pyrene intensity between the first and third vibronic peaks, i.e. I_1/I3, was calculated to determine the system's micropolarity in question. Figure 5 shows the I_1/I_3 values of the system as a function of cholesterol content.

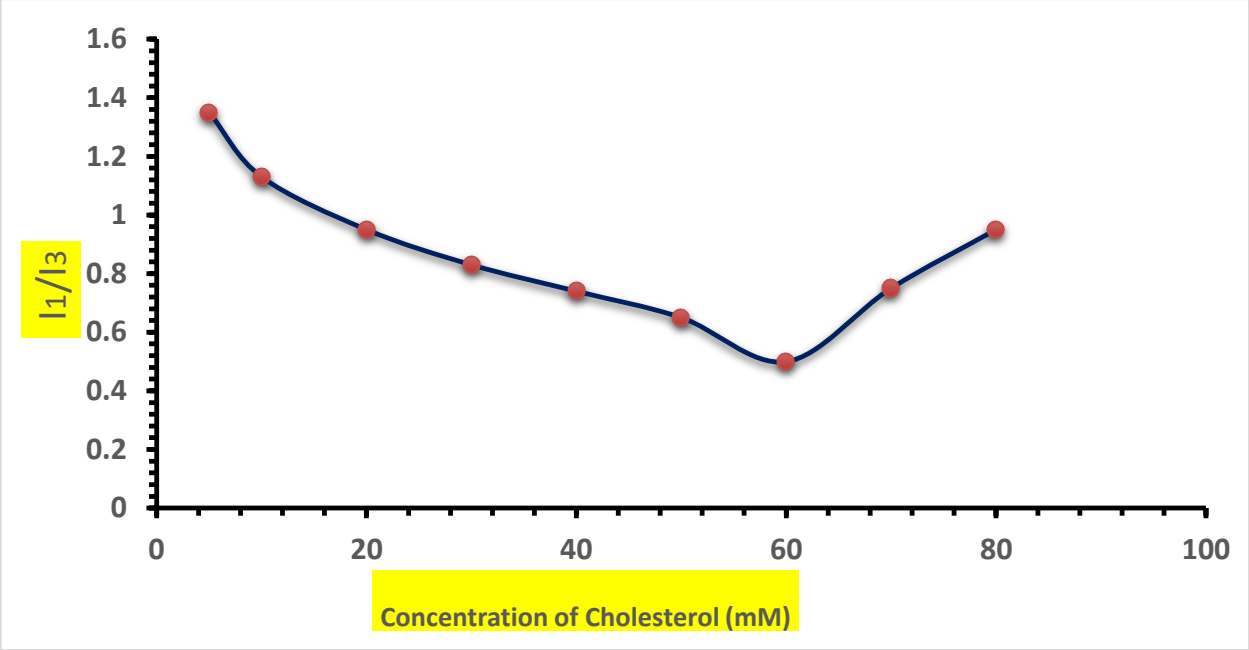


Fig.4 plot of I_1/I_3 of aqueous solution of 80 mM in the presence of increasing concentration of cholesterol the solid lines are guide to the eye

When the dipolarity of the pyrene cybotactic area is modified, The I_1/I_3 emission intensity ratio, which defines the pyrene solvent polarity scale, varies substantially. The much more polar the probe's atmosphere is, the greater the ratio, and vice versa. More vesicular aggregates in a solution are known to be more hydrophobic than micellar aggregates in a solution. As cholesterol concentration rises, I_1/I_3 tests demonstrate a clear decrease in the dipolarity seen by pyrene.

This could be due to the presence of cholesterol, which causes pyrene that is 'hydrophobic' is incorporated into the vesicle liposome. The surfactant system may be deduced from Figure 6's data. I_1/I_3 decreases with increasing cholesterol levels until a certain point, at which point it rises. For the examined system, the drop inside the graph that depicts the system's highest hydrophobic area is different. The pyrene concentration (60mM) at which it was exposed to the most hydrophobic environment. Apart from supra pyrene, which would be categorized into four fused benzene rings with out any functional group and has been accommodated in the most hydrophobic part of the vesicles, the bilayer, and has the least I_1/I_3 ratio, the data matches the turbidity and uv-vis absorbance data. The splitting up of the vesicular assembly into bigger aggregates, and also the spherical micelles, which seem to be a lower hydrophobic assembly than the vesicles, might explain the rise in hydrophobicity of the system after the fall. Turbidity, DLS (increased polydispersity), and uv-vis absorption investigations all confirm the conclusions, as previously stated.

SIZE OF THE AGGREGATES THROUGH DLS STUDIES

Figure 4 depicts aqueous amphiphile size distribution plots in the presence of varying amounts of cholesterol for the transitions (micelle-vesicle-micelle) and (micelle-vesicle-micelle). Micelle aggregates are the size of micellar solutions in amphiphiles (0mM) The size of the vesicle is (frequency percent 17.55, size 39.58 nm) at (50mM) concentration is (frequency percent 18.27, size 193.48 nm) and we get the micellar assembly again at (70 mM) concentration is (frequency percent 11.04, size 24.29 nm) correspondingly. The strength of light scattering is proportional to the sixth power of particle dimension, as per light scattering theory. smaller aggregates scatter more light than pristine amphiphilles[31]. The size and likely structure of the aggregates changes as the cholesterol concentration rises, as seen in Figure 4 for the common surfactant.

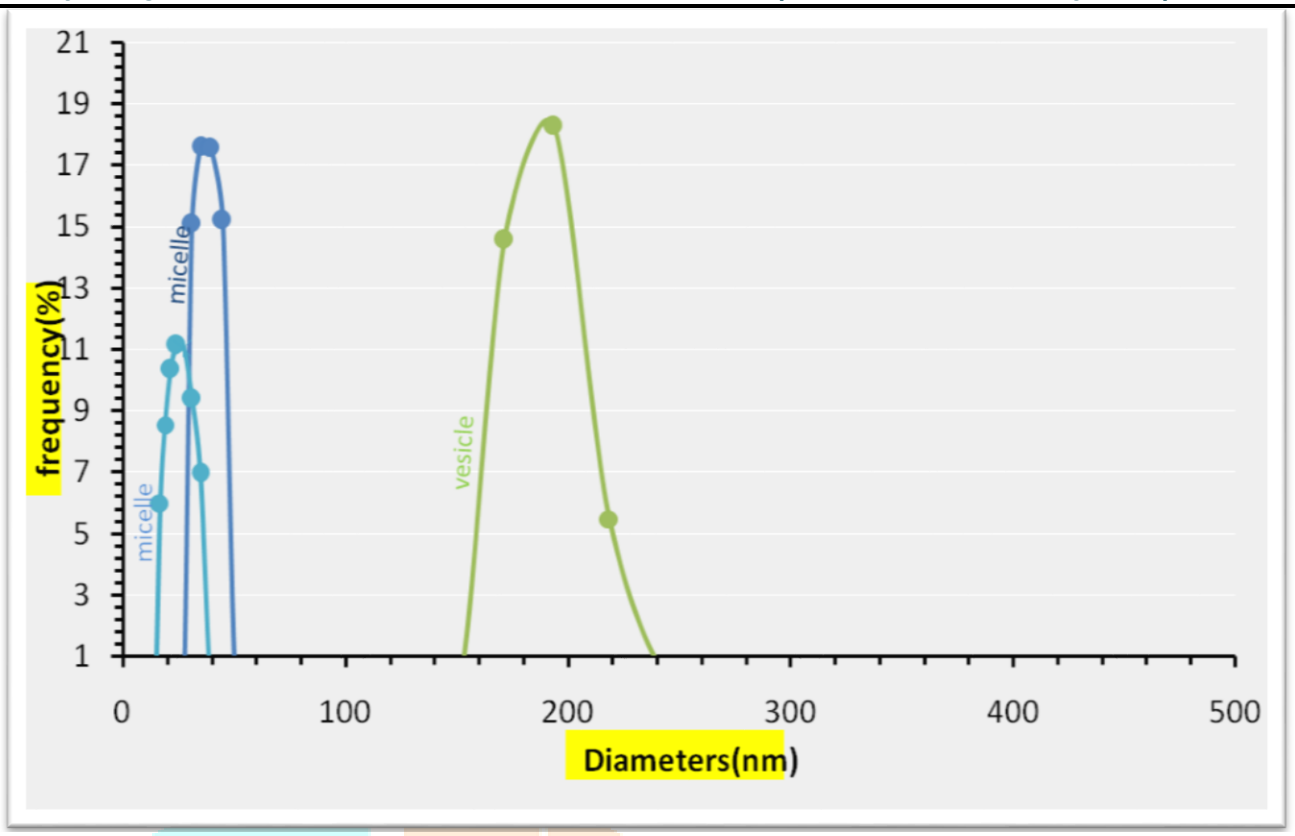


Fig.5 At various cholesterol concentrations, the size distribution of SDS/cho generating supramolecular assemblies.

With increasing concentrations from 0mM to 50mM, the occurrence of either mixed micelles or even a combination of micelles and vesicles[32] (cholesterol/sodium dodecyl sulphate) is indicated by the modest populations for sodium dodecyl sulphate of the bigger aggregates at lower cholesterol concentrations.The uniform unilamellar vesicles are segmented into bigger aggregates together with micelles was seen when the concentration of cholesterol increased from 50mM to 70mM.resulting in a skewed size distribution.
The aggregate size of SDS is larger, which may be due to the latter's enhanced surface activity [33]. The creation of bigger aggregates is caused by the high binding of cholesterol with SDS. The size of the aggregates which are most likely vesicles, is largely determined by the type of the amphiphiles head group and the amount of cholesterol supplied [34].

TRANSMISSION ELECTRON MICROSCOPY (TEM)

In the cholesterol/sodium dodecyl sulphate systems studied using turbidity and DLS methods, the micellar transition did not add to the understanding of the exact form and size of the aggregates,π but it did in TEM. Figure 4 shows TEM images of cholesterol/$NaC_{12}H_{25}SO_4$ mixtures with the same cholesterol (8 mM) and amphiphile concentrations (80 mM).

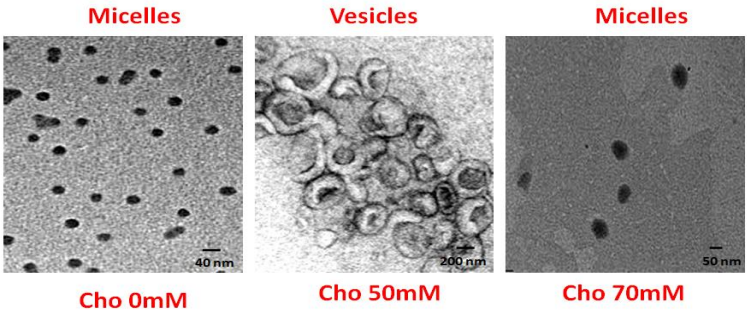


Fig.6 TEM images result of SDS/cholesterol with increasing concentration of cholesterol forming (micelles-vesicles-micelles)

The SDS system's TEM pictures reveal homogenous spherical unilamellar vesicles of various diameters. As we can see that at the (0mM) concentration the micelle starts forming and as we increase the concentration of cholesterol at (50mM) the vesicles are forming and as we increasing the concentration of cholesterol at (70mM)the vesicle breaks and again converted into micelles. The cholesterol/SDS mixture produced branched worm-like micelles as well as tiny unilamellar vesicles, as shown in fig.4. The vesicle bilayer in the system may be seen clearly. The system contains unilamellar vesicles as well as spherical aggregates of lesser sizes. as determined by the DLS measurement (see above). Furthermore, the size of the produced vesicles varies. The results are in line with those obtained from turbidity and DLS measurements. The creation of bigger aggregates for cholesterol/SDS is caused by cations-π and π-π interactions, as well as Hydrophobic interaction and hydrogen bond formation in between hydroxyl group of cholesterol and sodium dodecyl sulphate.

CONCLUSION

This study shows that cholesterol causes a micellar transition in the ubiquitous surfactant sodium dodecyl sulphate. The amount of cholesterol supplied and the surfactant's head group are the most important factors in morphological transformation. At a concentration of 20mM cholesterol, homogeneous lamellar vesicles were formed in a combination of cholesterol and sodium dodecyl sulphate. The amount of cholesterol necessary for the transition is larger than 20mM for a typical surfactant. Vesicles distorted into larger sized micelles as well as smaller sized spherical micelles with greater cholesterol concentrations. The hydrophobic interaction of SDS and cholesterol alkyl chains in aqueous media has been reported as a driving force for the formation of vesicles and micelle-vesicle-micelle transitions. Turbidity measurements and fluorescence spectroscopy studies, as well as DLS measurements and TEM pictures, are used to comprehensively describe vesicles. The results show that vesicles made from commonly used surfactants are stable. Based on the results of all experiments, lipid-induced microstructural changes in common surfactants reveal micelle-vesicle-micelle.

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