Abstract

Gemini surfactants are a new class of surfactants. They are made up of two identical or different amphiphilic moieties having the structure of conventional (monomeric) surfactants connected by a spacer group. At the outset, it must be emphasized that the spacer group must connect the two amphiphilic moieties at the level of, or in close vicinity to, the head groups. Spacer is the moiety which is responsible for the conversion of surfactants to gemini surfactants. There is variety of spacers i.e. the spacer may be hydrophobic (aliphatic or aromatic) or hydrophilic (polyether), short (two methylene groups) or long (up to 20 and more methylene groups), rigid (stilbene) or flexible (polymethylene chain). These new generation surfactants were coined as “Gemini surfactants” by Menger in 1991. The variety of gemini surfactants that have been synthesized to this day is already enormous with all kinds of spacer group. Gemini are known for their superior properties such as the low critical micelle concentration (cmc), high efficiency of reducing the surface tension of water, and micelle structural characteristics. Gemini surfactants are classified into four categories according to the nature of the hydrophilic head of the molecule or on the basis of sign of the charge they bear i.e anionic (carry negative charge), cationic (carry positive charge), zwitterionic (carry both charges viz negative and positive charge), and non-ionic (no charge). Out of these geminis, anionic geminis are used in grater volume than any other surfactant class. The potential applications that these properties suggested led to a renewed interest of the industrial community in these surfactants. Many surfactant-producing companies now have ongoing research on gemini surfactants. One company, Sasol (formerly Condea, located in Marl, Germany), is already offering formulations (Ceralution®) based on anionic gemini surfactants, which can be used as dispersing or
emulsifying agents, for foam production, and so forth. Anionic geminis are further sub
classified into four types i.e. sulphate, sulphonate, carboxylate and phosphate.

Phosphate gemini surfactants are a class of gemini surfactants. Phosphate
esters represent specialty surfactants fitting a number of niche markets. Beginning in the late
1950s, phosphate gemini surfactants found application as antistatic agents, emulsifiers,
wetting agents, and hydrotropes. Recently, surfactant market needs have demanded
materials possessing improved properties, especially low-irritation and mildness properties.
Because of their compatibility with skin and inherent low-irritation characteristics, these
species find use in personal-care applications, such as skin cleansers, body washes,
shampoos, and oral care formulations. Specifically, in skin irritation, skin roughness, and
skin tightness tests, monoalkyl phosphates exhibited superior performance when compared
to ether sulfates, sodium lauryl sulfate, soap and acyl L-glutamates. Besides this, the other
reasons for gaining importance were raw materials route and recovery. The easy availability
and non hazardousness of raw materials makes the preparation of phosphate gemini
surfactants superior. The simple route followed for the preparation of phosphate gemini
surfactants adds the excellencies of phosphate gemini surfactants. The yield or recovery was
also found to be better in case of phosphate gemini surfactants in comparison to others.

In the present course of work, an attempt has been made to prepare
phosphate gemini surfactants at 35 °C using the higher fatty alcohols namely tetradecanol
(C_{14}), hexadecanol (C_{16}) and octadecanol (C_{18}) with \( \alpha, \omega \)-alkyl dibromides (1, 4 DBB, 1, 6
DBH and 1, 8 DBO). The preparation of water soluble phosphate gemini surfactants is a
three step reaction. The first step of the reaction is the synthesis of mono alkyl phosphates
whereas, second step of the reaction comprises the synthesis of phosphate gemini
surfactants and third step is the synthesis of disodium salts of phosphate gemini surfactants. The effect of reaction variables like temperature and duration on the yield of mono alkyl phosphates was studied for the first of the reaction. The highest yield percentage of mono alkyl phosphates was obtained at 96h and 35 °C using 1:1 molar ratio of alcohols and pyrophosphoric acid. The influence of molar ratios of mono alkyl phosphates, tetramethyl ammonium hydroxide and α, ω-alkyl dibromides on the yield of phosphate gemini surfactants has also been reported and 1: 2: 0.5 molar ratio of mono alkyl phosphates, tetramethyl ammonium hydroxide and α, ω-alkyl dibromides was found to be optimum for the preparation phosphate gemini surfactants in highest yield irrespective of alcohols and α, ω-alkyl dibromides. The structures of synthesized phosphate gemini surfactants were verified by using modern analytical techniques viz. FT-IR, 1H NMR, and 13C NMR. Elemental analysis of synthesized bisphosphodiester surfactants was also carried out. Physico-chemical properties (foaming ability and stability, wetting ability, emulsifying ability, dispersing power and solubility) of synthesized gemini surfactants were also determined. Foaming ability and stability, wetting ability, emulsifying ability and dispersing power were observed to be increased with increase in the hydrophobic portion while, 1,6 DBH was predicted to be a better α, ω-alkyl dibromide regarding these properties whereas 1,8 DBO proved to be a better α, ω-alkyl dibromide for wetting ability. Apart from this anionic content of synthesized phosphate geminis was also evaluated and octadecanol based gemini surfactants having 1,6 DBH α, ω-alkyl dibromide showed maximum anionic content i.e. 80.7 %.

Surface active properties viz. surface tension, interfacial tension and critical micelle concentration was also carried out Experimental study revealed that for
higher alcohols comprising C_{14}-C_{18} chains, surface tension, interfacial tension and critical micelle concentration of aqueous solution of synthesized gemini surfactants increased with increase in hydrophobic chain length whereas decreased with increase in length of α, ω-alkyl dibromides.

Out of all the studied phosphate gemini surfactants, D,S-1,6-PGOD was found to be excellent on the basis of foaming ability and stability, emulsion stability, anionic content and dispersing power as compared to other synthesized phosphate gemini surfactants and D,S-1,8-PGOD was found to be superior with respect to the wetting ability, surface tension, interfacial tension and emc in comparison to others while D,S-1,4-PGTD was observed to be more soluble than other synthesized geminis.

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