Rheological response of methylcellulose toward alkanediyl-α,ω-bis(dimethylcetylammonium bromide) surfactants with varying spacer length

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ABSTRACT

The modulation of properties of methylcellulose (MC) by cationic gemini surfactants with varying spacer lengths was studied employing tensiometry, rheometry and turbidimetry. Surface tension measurements anticipate that the gemini surfactant with longer spacer chain length saturates MC at lower concentrations owing to its greater hydrophobicity compared to shorter spacer analogues. Rheometric and turbidimetric measurements suggest that at very low concentrations of gemini surfactants, ion-dipole type of interactions between MC and gemini surfactants promote the extension of polymer chains which is manifested by an initial increase in the low shear viscosity and gelation temperature of MC–gemini surfactant systems, and lowering of turbidity. Such interactions were found to be stronger in case of 16-4-16 than 16-5-16, and almost absent in case of 16-6-16. However at concentrations above CAC, hydrophobic forces operative between MC and gemini surfactants were found to be more for 16-6-16 than that of 16-5-16 and 16-4-16. The final levelling of MC viscosity in presence of all the three gemini surfactants and the variation of gelation temperature suggests the solubilization of network junctions in the surfactant micelles. Moreover, the presence of gemini surfactant strongly affects the interaction of MC with a model hydrophobic drug rifampicin.The results highlight the importance of gemini surfactants and their spacer length in controlling the structural dynamics of MC and its effective use in pharmaceutical and food industry.

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1. Introduction

Cellulose based water soluble polymers have been extensively used as drug delivery vehicles and excipient for enhancing the stability of drug formulations in pharmaceutical industry (Sardar, Ali, Kamil, & Kabir-ud-Din, 2010), viscosity modifiers or gelling agents in food stuffs and cosmetic products, thickeners in water based paints and as protective colloids in polymerization processes (Kastner, Hoffmann, Donges, & Ehrler 1996). Methylcellulose (MC) is rendered soluble by substitution of hydroxyl groups in cellulose with methoxyl groups. This modification of cellulose is expressed as the Degree of Substitution (DS) and is defined as the number of methoxyl groups divided by the number of glucose units in cellulose, whose value should neither be too low nor too high. This is because MC is insoluble in water both at high and low values of DS owing to hydrogen bonding and hydrophobicity respectively. At intermediate DS, ca. 1.7–2.0 (Kobayashi, Huang, & Lodge, 1999), MC is water soluble and hence used in various commercial products.

MC is known to form temporary hydrophobic association networks in aqueous medium, which tends to minimize their exposure towards water (Desbrières, Hirrien, & Ross-Murphy, 2000). The addition of surfactants affects their association behaviour which is manifested as changes in the properties like viscosity, gelation temperature, etc. In semi-dilute polymer solutions in the presence of the moderate surfactant concentrations, the intermolecular hydrophobic interactions are enhanced giving rise to gel like networks showing a significant increase in solution viscosity than that of pure hydrophobically modified (HM) polymer solutions. A further increase in surfactant concentration results in the masking of the hydrophobic groups thereby decreasing intermolecular interactions and consequent network breaking and lowering of viscosity, even lower than that of surfactant free solution (Bai, Khin, Chen, Tsai, & Chen, 2005). The thermoreversible gelation of cel-

lulose based polymers is a well-documented subject in literature (Desbrières et al., 2000; Hussain, Keary, & Craig, 2002; Kobayashi, Huang, & Lodge, 1999; Li, 2002). Anionic surfactants have been found to interact strongly with water soluble HM non-ionic polymers compared to cationic surfactants (Mir, Dar, Amin, & Rather, 2009; Panmai, Purd'homme, & Peiffer, 1999; Piculell, Egermayer, & Sjöström, 2003; Wang and Olofsson, 1995). It has been ascribed to the bulkiness of the cationic head group and electrostatic repulsion between protonated polymer in water and surfactant head group, in addition to the hydration shell of the polymer which does not favour interactions with cationic head groups (Mir et al., 2009).

Gemini surfactants are composed of two amphiphilic moieties covalently connected at head groups or near to it by a spacer group (Han and Wang, 2011; Zana, 2002). Such surfactants have critical micelle concentration (CMC) one or two orders of magnitude lower than corresponding conventional surfactants, better surface activity and wetting properties related to the bimodal distribution of head groups in micelles formed by these surfactants (Zana, 2002). Chain length and spacer group play a pivotal role in deciding the properties of gemini surfactants. Menger and Littau (1991) observed an unusually high CMC for a longer chained surfactant than the shorter one, which they attributed to the formation of premicellar aggregates by the long chained surfactant. Cationic gemini surfactants with polymethylene spacer group [alkanediyl-α,ω-bis(alkyldimethylammonium bromide)] display odd–even effect in enthalpy of micellization (ΔH_{mic}) with the number of carbon atoms in hydrophobic chains; endothermic for surfactants with odd numbered chains, and exothermic for surfactants with even numbered chains except the surfactant having eight carbon long alkyl chain (Li et al., 2005). Both nature and length of the spacer have an effect on the physicochemical properties of the gemini surfactants. CMC values of gemini surfactants with a hydrophobic polymethylene spacer (such as those used in our study) go through a maximum as the spacer becomes 5 or 6 carbon atoms long, while as in surfactants with hydrophilic poly(ethylene oxide) spacer, instead of a maximum, slow and monotonous increase is observed (Han and Wang, 2011).

There have been a lot of studies on surfactant–polymer systems employing conventional single chain surfactants and cellulose based polymers (Bai et al., 2005; Beheshti, Nguyen, Kjøniksen, Knudsen, & Nyström, 2006; Chakraborty, Chakraborty, & Ghosh, 2006; Dar, Garai, Das, & Ghosh, 2010; Guillot, Delsanti, Desert, & Langevin, 2003; Guillot, McLoughlin, Jain, Delsanti, & Langevin, 2003; Hoff, Nyström, & Lindman, 2001; Kundu and Kundu, 2001; Lund, Lauten, Nyström, & Lindman, 2001; Mata, Patel, Jain, Ghosh, & Bahadur, 2006; Nilsson, Thuresson, Hansson, & Lindman, 1998; Panmai, Prud'homme, Peiffer, Jockusch, & Turro, 2002; Piculell et al., 2003; Silva, Antunes, Sousa, Valente, & Pais, 2011; Tanaka, Meadows, Williams, & Phillips, 1992; Villetti et al., 2011; Wang, Li, Liu, Xu, & Liu, 2006; Winnik and Winnik, 1990). The effect of hydrophobic salts (Dar et al., 2010) and conventional surfactants on the viscosity and gelation of MC solutions (Kundu and Kundu, 2001; Villetti et al., 2011; Wang et al., 2006) have been reported. However, the effect of gemini surfactants on the properties of cellulose based polymers is scarcely explored and deserves attention. In MC, two types of interactions with cationic gemini surfactants arise-hydrophobic interactions between surfactant tails and hydrophobic segments of MC, and ion–dipole interaction between cationic head groups and polar moieties of MC (Bao, Li, Gan, & Zhang, 2008). Therefore, studying physicochemical properties of MC and gelation in presence of different concentrations of cationic gemini surfactants of varying spacer lengths could be helpful in gaining insight into effect of dimeric surfactants on non-ionic polymer. Since gemini surfactants are known to have better surface properties in comparison to the conventional surfactants and that the raw material for obtaining MC is abundant in nature,

MC–gemini surfactant systems are expected to be potential candidates to be used for various industrial processes. This paper aims to gain an insight into the interactions of MC with gemini surfactants which has been ignored so far.

2. Experimental

2.1. Materials

MC, with the trade name of Methocel A4C, was product of Dow Chemical Company with number average molecular weight of 41,000 g mol⁻¹. The average degree of methoxyl substitution (DS) of MC was calculated by ^{1}H NMR spectroscopy (Supplementary information) and was found to be 1.8. Prior to use, the MC was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature. Gemini surfactants $C_{16}H_{33}N^+(CH_3)_2$–$(CH_2)_s$–$N^+(CH_3)_2C_{16}H_{33}$, 2Br⁻ with s = 4–6 indicating the length of the spacer chain (16-4-16, 16-5-16, 16-6-16), were synthesized as per the procedure described in literature (Kabir-ud-Din, Siddiqui, Kumar, & Dar, 2006). Rifampicin ($\geq$97%) was purchased from Himedia, India.

2.2. Surface tension measurements

Surface tension measurements were made on a Kruss K9 tensiometer using platinum ring detachment method, having an accuracy of $\pm$0.1 mNm⁻¹. For pure surfactant systems, 20 mL of triply distilled water was taken in a pan and known volumes (30 μL) from surfactant stock were added and surface tension measurements were made. For surfactant–polymer systems, 20 mL of 1% MC solution (prepared by dissolving 1 g of MC in 75 mL cold water and making the total volume to 100 mL The solution was used after equilibration of 48 h at a temperature of 4 °C) was taken in a pan and 30 μL of surfactant stock solution were progressively added. Temperature was kept constant at 25 °C by employing Brooke Field water bath accurate to $\pm$0.1 °C.

2.3. Rheology

Anton Paar modular compact rheometer (MCR 102) having peltier based temperature control system with accuracy of $\pm$0.01 °C was used for rheological measurements. For studying the variation of viscosity as a function of shear rate, rotational method employing cone and plate geometry (diameter of 50 mm with cone angle of 1°) was employed in which shear rate was varied from 0.1 s⁻¹ to 100 s⁻¹. The effect of gemini surfactants on gelation temperature of MC was studied by oscillatory method employing parallel plate geometry (PP-40) at a constant frequency of 1 Hz and a low shear amplitude (10%) to ensure that the measurements were performed in a linear viscoelastic region in which the dynamic storage moduli are independent of the applied stress. Temperature was varied from 20 °C to 80 °C at the rate of 1 °C per min. The temperature at which an abrupt increase in storage modulus occurs was taken as gelation temperature.

2.4. Spectrophotometry

WSP-UV-580PC spectrophotometer equipped with a HAAKE GH water bath of $\pm$0.1 °C accuracy was used for turbidimetric and drug interaction studies by employing quartz cuvette of 10 mm path length. All the experiments were carried out at 25 °C.

(a) Turbidimetric measurements

Turbidimetric experiments were carried out by placing 1% MC + gemini surfactants in cuvette, and the data was obtained in transmittance mode at 300 nm and plotted as 100-%transmittance versus [gemini surfactant].