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Preservative solubilization induces microstructural change of Triton X-100 micelles

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ABSTRACT

The interaction of preservatives which are extensively used in food, pharmaceutical and personal care products, such as p-hydroxy benzoic acid esters (parabens) and gallic acid ester for instance propyl gallate has been investigated with commonly used non-ionic surfactant p-tert-octylphenoxy polyethylene (9.5) ether, Triton X-100 (TX-100). Solubilization of these preservatives alters the micellar behaviour of TX-100 elucidated by cloud point (CP), viscometry, dynamic light scattering (DLS), small angle neutron scattering (SANS) and NOESY measurement techniques. The changes in size/shape of TX-100 micelles depend on the hydrophilic and hydrophobic interactions with preservatives. These types of interaction facilitate the site of solubilization of preservatives in TX-100 micelles. Micellar growth of TX-100 was more pronounced for parabens as their alkyl ester chain length increases. Moreover, the micellar growth was more prominent for propyl paraben (PP) as compared to more polar propyl gallate (PG). The salt induced changes in the interaction between preservatives and TX-100 micelles have also been determined.

1. Introduction

Parabens and gallates are well known preservatives which have long been used in industries for detaining or preventing the progress of oxidative deterioration because of their wide-ranging antimicrobial/antifungal activity, stability and aqueous solubility [1–4]. Hence, these preservatives are extensively utilized as antioxidants in personal care products [1,5], pharmaceuticals [6], foodstuffs [7,8] and beverages [9]. Generally, parabens and gallates work in the aqueous medium and their solubilities can be altered in the presence of surfactants. Moreover, the preservative activity of the parabens and gallates significantly depends on their degree of bindings with surfactants [10–12]. Furthermore, such preservatives alter the micellar properties of aqueous surfactant systems [13,14]. Therefore, our interest has been centred to study the interaction between preservatives and surfactants in consideration of its probable application as preservatives in surfactant based formulations. Several articles have been published relating the possible mechanism of the interaction of parabens and gallates with surfactants [10–20]. Solubilization studies of parabens have been investigated in the aqueous solutions of polyoxyethylene type nonionic surfactants [11,15,18,20] and anionic surfactant, sodium dodecyl sulphate (SDS) [12,20]. The solubilization sites of parabens and PG in the surfactant micelles have been examined using fluorescence probe and ^{1}H NMR methods [11,16]. Heins et al. [17] have determined that the antioxidant activity of gallates depends on their solubilization sites in micelles using electron spin resonance (ESR) technique and concluded that cetyltrimethylammonium bromide (CTAB) and Polyoxyethylene (20) cetyl ether (Brij 58) provide more antioxidant activity to gallates than SDS.

Several studies have illustrated that parabens and their salts are efficient to change the geometry of surfactant micelles [13,14,21]. Khimani et al. [13] examined the different solubilization effects of methyl and butyl parabens in pluronic micelles using small angle neutron scattering (SANS). They observed that methyl paraben (MP) leads to sphere to rod micellar transition for both hydrophobic pluronic (P103) and moderately hydrophobic pluronics (P104, P105). However, butyl paraben (BP) offers the same effect for P103, but formed micellar clusters for P104 and P105 due to the inception of inter-micellar interaction. Paraben induced moderate growth of hydrophilic pluronic F127 micelles has been reported using SANS [14]. Kroflic et al. [21] studied ethyl paraben sodium salt induced elongated micelles of dodecyltrimethylammonium chloride (DTAC) with higher aggregation number whereas less hydrophobic methyl paraben sodium salt did not show such type of effect.

Parabens and gallates are widely used preservatives, but they are harmful to human and animals. Parabens and gallates have been reported as endocrine disruptors and reproductive toxic [4,22,23], allergens [5,24] to humans and toxic to aquatic organisms [25,26]. Therefore, several authors have investigated green and less costly cloud point extraction (CPE) method using polyoxyethylated nonionic surfactants for separation of these types of preservatives [27–30].

Non-ionic surfactants represent an important class of amphiphiles among which Triton X series surfactants have been extensively employed in industrial and domestic fields [31]. These surfactants

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have been extensively studied for the solubilization of aromatic hydrocarbons [32–35], pesticides [36,37], phenols [38,39] and nitrotoluenes [40]. Moreover, these surfactants are used widely for the removal of hazardous substances like dyes [41,42], pesticides [43], phenols [44], and heavy metals [45] by CPE method. Our research group has investigated the locus of solubilization of phenols [38,39], aromatic acids [46], aromatic amine [47], alcohols and glycol ethers [48] and their effect considering pH, temperature and hydrophobicity on micellar characteristics of Triton X-100 (TX-100) using spectral and scattering methods. Nevertheless, the interaction of parabens and gallates with Triton X series surfactants in aqueous media and resulting micellar properties have been not studied yet. For that reason, we have investigated the effect of a homologous series on the length of the alkyl chain esters of chemicals that include methyl- (MP), ethyl- (EP), propyl- (PP), butyl- (BP), and benzyl parabens (BzP) on the micellar behaviour of TX-100. The effect of propyl paraben was compared with more hydrophilic propyl gallate (PG). The presence of salts has been found to alter the interaction between additive and TX-100 in aqueous media. We carried out cloud point, viscosity, DLS, SANS and NOESY experiments to invent the solubilization and locus induced morphological changes of TX-100 micelles.

2. Material and methods

Triton X-100 (TX-100) was purchased from Sigma-Aldrich and used without further purification. Methyl paraben (MP), ethyl paraben (EP), propyl paraben (PP), butyl paraben (BP) and benzyl paraben (BzP) were also obtained from Sigma-Aldrich and used as received. Propyl gallate (PG) was purchased from SRL (India) and used without further purification.

2.1. Cloud point (CP)

The cloud point (CP) was determined at a fixed concentration of TX-100 (5 wt.%) at varying concentrations of parabens and gallate by gradually heating solutions in thin glass tubes immersed in a stirred heating bath. The CP has been considered as sudden attendance of turbidity in the solution by gradual increase in the temperature. The CP values were consistent within 0.5 °C.

2.2. Viscosity

The viscosity measurements were achieved in a temperature controlled water bath with constancy of ± 0.1 °C. Calibrated Cannon Ubbelohde viscometers have been used with sizes 25 and 100 having constants 0.001869 and 0.01610 $cSts^{-1}$, respectively. The variation in flow time was found to be ± 5 s. Initially absolute viscosities of the solutions were obtained which were multiplied by viscometer constant to get kinematic viscosity in centistokes. Then viscosities in centipoise have been obtained by the multiplying the kinematic viscosity with density of solvent (water). These viscosities of solutions were divided by viscosity of water to obtain the relative viscosity (η_{rel}) [38].

2.3. Dynamic light scattering (DLS)

The DLS experiments were carried out at a fixed scattering angle of 90° and wave length of 633 nm using Zeta sizer Nano-ZS 4800 (Malvern Instruments, UK) having He–Ne laser. Each measurement was repeated at least three times. The apparent hydrodynamic radius (R_h) of the micelles was calculated using the Stokes–Einstein equation. All samples were prepared in Millipore water and filtered through a 0.45 μm filter to avoid dust particles.

2.4. Turbidimetry

Different solutions were prepared containing 5% TX-100 and PG concentration range of 0–55 mM in water, 1 M NaCl and 1 M NaI solutions. The transmittance (%T) was measured for these solutions after agitating for 24 h. Transmittance was measured at 420 nm by UV–Visible spectrophotometer (Thermo Scientific TM Evolution 300). The transmittance has been converted to turbidity by using formula of 100 − %T [34].

2.5. Small angle neutron scattering (SANS)

The SANS measurements were carried out using a SANS diffractometer at the Dhruva reactor, BARC, Trombay. For SANS measurements, all the solutions were prepared in D_2O. Q range of 0.017–0.35 Å has been used for the scattering measurements. Data were corrected for background, empty-cell influence and sample transmission, and normalized to absolute cross-section units. The fitted parameters in the analysis were optimized using non-linear least square fitting programme to the model scattering. The detailed procedure of experiments can be found elsewhere [38,46].

2.6. Nuclear magnetic resonance

2D NMR (NOESY) experiments were performed on a Bruker AVANCE-II 400 MHz spectrometer at St. Fx University Canada. Samples were prepared in D_2O. The spectrum was calibrated by setting the HDO peak at a chemical shift of 4.65 ppm at 298 K. The HDO peak due to residual water was eliminated by solvent suppression techniques. All measurements were performed at 30 °C.

3. Results and discussion

Parabens possess a common aromatic ring, –OH group but different alkyl/aryl groups which define their solubility and play an important role in interaction with surfactant micelles. The structure, solubility and octanol–water partition coefficient ($P_{o/w}$) of different parabens and propyl gallates used are shown in Scheme 1 and Table 1. A high $P_{o/w,}$ is likely to exhibit significant penetration in micellar phase [39, 48], while low $P_{o/w}$ value indicates that the compound remains more in aqueous bulk phase than the micellar phase.

The effects of nature and concentration of these additives on phase behaviour and micellar characteristics of aqueous solution of TX-100 made from turbidimetric, scattering (DLS and SANS) and viscosity are discussed below. The interaction between the propyl paraben/gallate and TX-100 is also discussed by NOESY.

3.1. Effect of additive concentration

Fundamental information regarding the interaction of preservatives with TX-100 micelles was obtained by the measurements of CP and relative viscosity. These measurements were carried out by keeping fixed concentration of TX-100 (5%) and varying concentrations of the additives. For nonionic surfactant CP is an important parameter which is very sensitive in the presence of additives even at very low concentrations [48–50]. If an additive alters CP of surfactant, it indicates changes in interaction between water and surfactant which result in changes in micellar size/shape. Changes in microstructure of micelles also lead to changes in solution viscosity. Fig. 1 shows CP, relative viscosity (η_{rel}) and hydrodynamic diameter (R_h) of 5% TX-100 micellar solution as a function of concentration of different additives viz. MP, EP, PP, BP and BzP. Results indicate that all additives decrease the CP and increase in viscosity of TX-100 solution but in different manners. It has been noticed that as the length of the hydrocarbon chain of paraben increases from MP to BP, the CP decreases while viscosity and micellar radius increase. BzP was also efficient and provides greater changes in micellar behaviour of TX-100 as compared to alkyl parabens.