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Topographical and photophysical properties of poly(amidoamine) dendrimers with ionic surfactants

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Abstract

The atomic force microscopy (AFM) and transmission electron microscopy (TEM) have been performed on the poly(amidoamine) dendrimers of second generation (2G) and its fluoroderivative (2D) at room temperature. Both studies have demonstrated that 2G and 2D exist in large aggregates on solid surface. The presence of ionic surfactants facilitates their solubilization in micellar phase resulting in the aggregates of much smaller dimensions. The aqueous bulk properties of 2G and 2D both in the absence as well as in the presence of ionic surfactants (i.e. dodecyltrimethylammonium bromide (DTAB), dimethylene bis (dodecyldimethylammonium bromide) (12-2-12), and sodium dodecyl sulfate (SDS)) have been carried out with the help of pyrene fluorescence and turbidity (τ) measurements. From the variation of I_1/I_3 pyrene intensity and the τ of these aqueous solutions, it has been found that both DTAB and 12-2-12 interact with the surface groups of 2G and 2D favorably in basic medium, while SDS has been found to interact with that in acidic medium. Apart from this, interactions of cationic surfactants have been found to be stronger with 2D in comparison to 2G, while reverse has been observed in the case of SDS.

Keywords: Poly(amidoamine) dendrimers; Ionic surfactant; Topographical and photophysical properties; Dendrimer–surfactant aggregates; pH effect

1. Introduction

During the last decade, the poly(amidoamine) dendrimers (PAMAM) have fetched a considerable importance due to its readily water soluble nature. The physicochemical aspects of these macromolecules have been evaluated with a variety of techniques [1–13]. The contrasting spherical nature of these polymers from that of conventional linear polymers have generated tremendous scope in evaluating the fundamental properties both in the homogeneous as well as in the heterogeneous media [14–18]. Several studies have reported their interactions with conventional ionic surfactants and found that anionic surfactants interact much strongly than cationic surfactants [19,20]. Apart from this, the nanopaticles formation in the presence of these PAMAM have also been reported [21] even without the use of reductant. The PAMAM macromolecules have been found to reduce the metal salt to generate metal nanoparticles loaded with dendritic macromolecules.

In the present study, we have selected second generation of PAMAM (2G) and its fluoroderivative (2D) (Scheme 1) to study their interactions with different kinds of surfactants such as sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), and dimethylene bis (dodecyldimethylammonium bromide) (12-2-12) in neutral, acidic, and basic media. Both 2G and 2D are expected to aggregate in aqueous phase and their aggregation processes have been studied with the help of AFM and TEM measurements.

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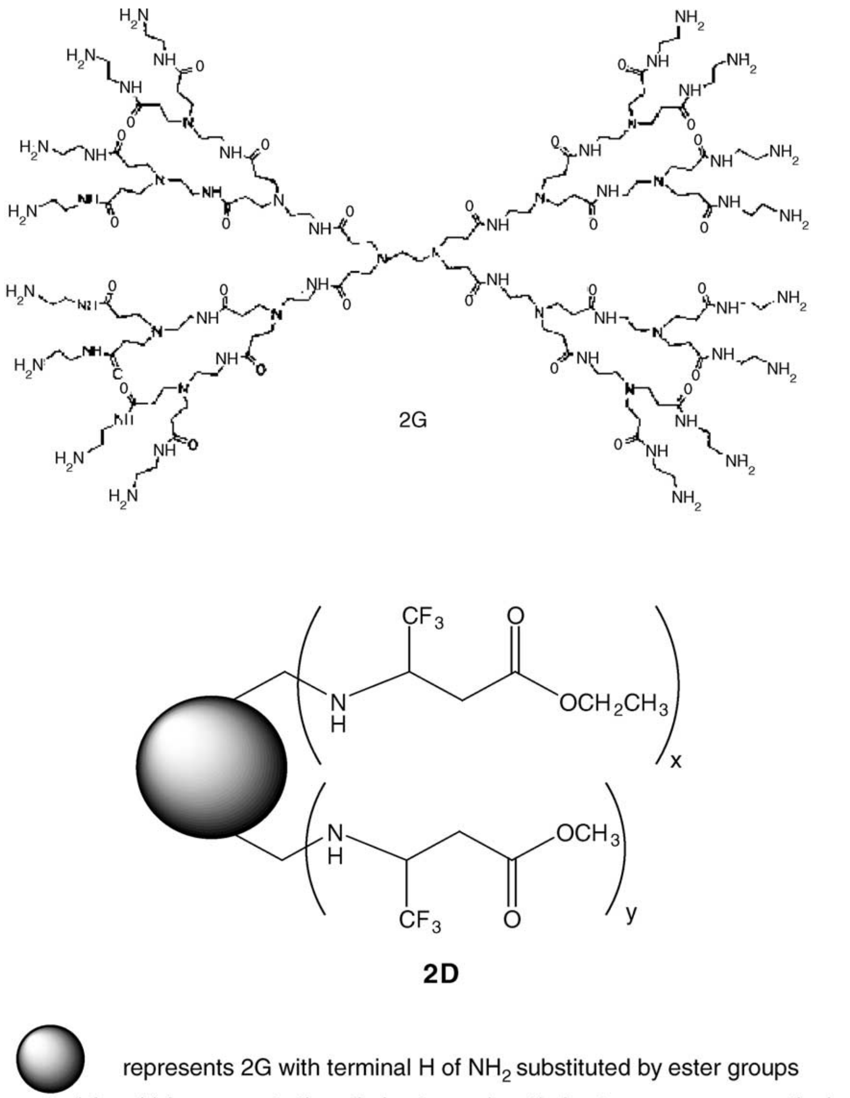

represents 2G with terminal H of NH_2 substituted by ester groups
'x' and 'y' represents the ethyl ester and methyl ester groups, respectively.

Scheme 1.

In the solution phase, this aggregation behavior is expected to influence their interactions with present ionic surfactants and hence, experiments have been performed in acidic, basic, and neutral media. The selection of different ionic surfactants would help us to evaluate the dependence of PAMAM–surfactant interactions on the basis of different nature of surfactant head groups as well as hydrophobic tails.

2. Experimental

2.1. Materials

Poly(amidoamine) dendrimer (2G) was synthesized by means of procedure described by Tomalia et al. [22] where ethylenediamine was used as a nitrogen core and fully characterized by IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopy before use. The fluoroderivative (2D) was synthesized as reported [23] in the literature and was fully characterized by ^{1}H NMR. The molecular structures of both 2G and 2D have been shown in Scheme 1. Dimethylene bis (dodecyldimethylammonium bromide) was synthesized according to the method reported elsewhere [24]. Dodecyltrimetylammonium bromide was synthesized as follows: 1-bromododecane was refluxed (80 °C) in the presence of 5–10% excess trimethylamine in dry ethanol for 48 h. The excess trimethylamine was used to ensure the completion of reaction. The surfactant thus synthesized was recrystallised several times from acetone. The purity of the surfactant was checked by ^{1}H NMR using a Brucker AC 200E instrument. ^{1}H NMR ($CDCl_3$) δ_H: 3.60 (2H, t, $-NCH_2-$), 3.49 (9H, s, $-NCH_3$), 1.43 (20H, m, $-(CH_2)_{10}-$), 0.90 (3H, t, $-CH_3$).

Sodium dodecyl sulfate 99%, from Aldrich, used as received.