

Molecular Encapsulation and Ion-Transfer Behavior of Carboxy-Terminated PAMAM Dendrimer at the Liquid/Liquid Interface

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Introduction

The ion-partition behavior of various organic species at the liquid/liquid interface between immiscible aqueous and organic solutions has been examined as a biomimetic reaction system. Dendrimers are nontraditional polymers with well-defined structure consisting of a core, iterative branch units, and terminal groups. Because of spherical molecular shape and a large number of functional groups, dendrimers have been demonstrated to be capable of encapsulating the organic molecules and applied to the drug delivery system. In this work, the molecular encapsulation and interfacial behavior of generation 3.5 polyamidoamine (G3.5 PAMAM) dendrimer was studied by means of spectro-electrochemical techniques.

Experimental

The interfacial mechanism of G3.5 PAMAM dendrimer in the presence of anilino-naphthalene derivatives, 8-anilino-1-naphthalenesulfonate (ANS) and bis-ANS, was studied by potential-modulated fluorescence (PMF) spectroscopy.^{1,2} The fluorescence intensity from the interfacial region was analyzed as a function of the perturbation of the Galvani potential difference ($\Delta_o^w \phi \equiv \phi^w - \phi^o$).

Results and Discussions

Anilino-naphthalene derivatives are sensitive to the polarity of media, in which

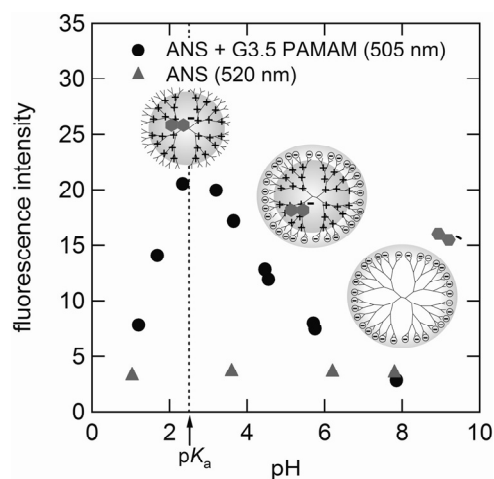


Fig. 1 Fluorescence intensity of ANS in the presence and absence of G3.5 PAMAM dendrimer. The excitation wavelength was 410 nm. The concentrations of G3.5 PAMAM dendrimer and ANS in the aqueous phase were 50 μ M, respectively.

the fluorescence quantum yield increased in less polar medium. As ANS (or bis-ANS) is encapsulated in the dendrimer, the fluorescence intensity is significantly enhanced in comparison with it in the bulk aqueous phase. The fluorescence intensity of ANS was increased in the presence of G3.5 PAMAM dendrimer at pHs less than 6 where the dendrimer exists as a cationic form (**Fig. 1**). It indicates that the anionic ANS was electrostatically encapsulated into the positively-charged interior of the dendrimer. At pH lower than pK_a of ANS, the electrostatic interaction with the dendrimer and the corresponding fluorescence enhancement were considerably decreased.

The potential dependences of the molecular encapsulation and the interfacial mechanism were investigated by PMF measurements. In the acidic condition, the PMF responses demonstrate that the dendrimer stably incorporates the ANS anion in the bulk phases at the positively polarized interface (**Fig. 2**). On the other hand, ANS is released from the dendrimer and transferred across the interface at ca. 0 V. The frequency response analysis of PMF signals indicated that the ion-transfer process of the dendrimer is accompanied by the adsorption step (**Fig. 3**). Bis-ANS exhibited similar spectro-electrochemical responses. The strong interaction between bis-ANS and the dendrimer was also confirmed by a negative-shift of the ion-transfer potential. The molecular encapsulation and the interfacial mechanism of G3.5 PAMAM dendrimer will be discussed in terms of the electrostatic interaction and the molecular size of guest molecules.

References

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2. H. Nagatani, T. Ueno, T. Sagara, *Electrochim. Acta*, **53(22)**, 6428 (2008).

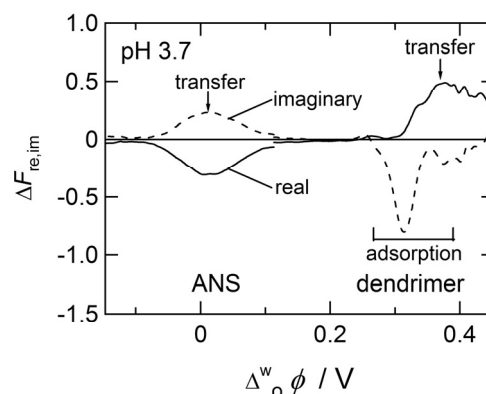


Fig. 2 Potential dependence of PMF in the presence of G3.5 PAMAM dendrimer and ANS at 1.0 Hz. The excitation and the emission wavelengths were 410 nm and 505 nm, respectively. The concentrations of G3.5 PAMAM dendrimer and ANS were 50 μ M, respectively.

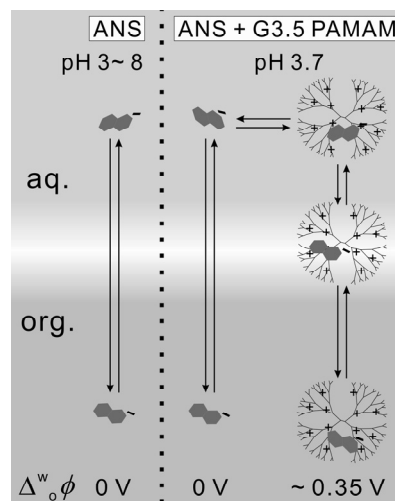


Fig. 3 Schematic representation of G3.5 PAMAM dendrimer and ANS at the water/DCE interface.