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Spectroelectrochemical analysis of ion-transfer and adsorption of the PAMAM dendrimer at a polarized liquid|liquid interface

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ABSTRACT

The interfacial behavior of the fourth generation polyamidoamine (G4 PAMAM) dendrimer at a water|1,2-dichloroethane (DCE) interface was studied by cyclic voltammetry and potential modulated fluorescence (PMF) spectroscopy. Irregular voltammetric responses were observed at positively polarized interfaces. The cyclic voltammogram was strongly dependent on pH and on the concentrations of the G4 PAMAM dendrimer and the organic supporting electrolyte. PMF spectroscopy was successfully used to analyze the interfacial mechanism of the dendrimer by adding an anionic porphyrin derivative as a fluorescent probe. The results of the PMF measurements demonstrated that the G4 PAMAM dendrimer was transferred across the interface, a process that was accompanied by an adsorption step at pH 7. In contrast, under alkaline conditions, the adsorption process did not seem to be involved in the interfacial behavior.

1. Introduction

Dendrimers are unique and nontraditional polymers with a well-defined macromolecular architecture consisting of a core, iterative branch units, and terminal groups [1]. Dendrimers have been demonstrated to be capable of encapsulating various organic molecules, and their application to drug delivery systems has been studied extensively [2,3]. A full generation polyamidoamine (PAMAM) dendrimer is constructed based on an ethylenediamine core and terminated with amino groups. The fourth or higher generation PAMAM dendrimers are approximately spherical molecules. The periphery region secludes the organic species captured in the interior from the solution phase, making higher generation PAMAM dendrimers very useful as molecular capsules (or containers). The net charge on a dendrimer molecule is determined by the protonation of the terminal amino groups and tertiary amines of the branch unit, while the intramolecular charge repulsion induces the conformational change [4,5]. The electrode potentials also contribute to the conformational change of the dendrimer molecules adsorbed on the electrode surface [6,7]. Recently, Arrigan and coworkers reported the fundamental electrochemical behavior of poly(propylenimine) and PAMAM dendrimers at the liquid|liquid interface [8]. The voltammetric responses indicated complex irreversible behavior for the third generation PAMAM dendrimer.

The liquid|liquid interface is specific two-dimensional reaction field used in separation sciences, nanomaterials formation, and the self-assembling of supramolecules [9]. The ion-partitioning and distribution properties of organic species have also been examined at the interface as a model of biomembrane systems by means of ion-transfer voltammetry. The transfer of ionic species across the interface often involves the adsorption process [10–12] and follows the ion-association of adsorbed monomer species [13,14]. Elucidation of the potential-dependent adsorption behavior would be a key point to understand the ion-transfer mechanism.

In this work, the interfacial behavior of the fourth generation (G4) PAMAM dendrimer was investigated at the water|1,2-dichloroethane (DCE) interface under potentiostatic control. The G4 PAMAM dendrimer exhibited irregular voltammetric responses at positively polarized interfaces. Potential modulated fluorescence (PMF) spectroscopy was employed in order to reveal the interfacial transfer mechanism of the dendrimer in detail. The PMF results demonstrated the pH dependence of the interfacial behavior of the positively charged dendrimer molecule.

2. Experimental

The G4 PAMAM dendrimer, schematically shown in Fig. 1, was purchased from Aldrich (10 wt% in methanol) and prepared as an aqueous solution after removing the methanol by drying in argon

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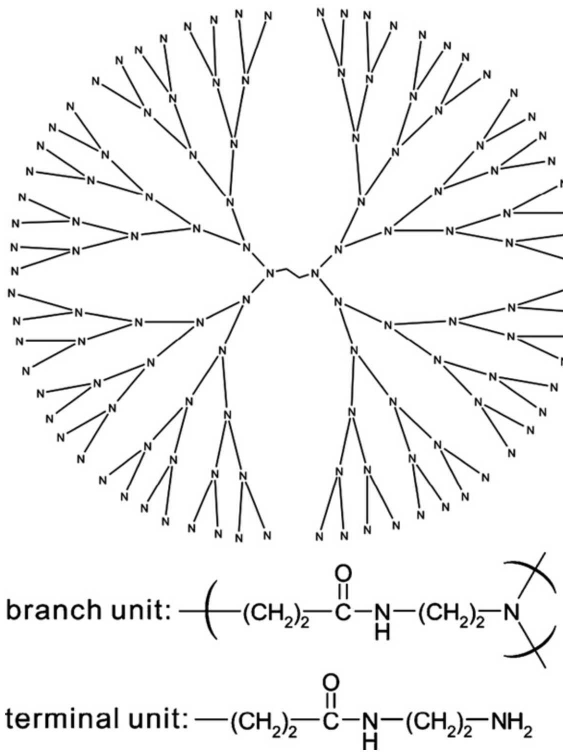

Fig. 1. Schematic drawing of the molecular structure of the G4 PAMAM dendrimer.

gas. The composition of the electrochemical cell is represented in Cell I.

Ag	AgCl	1×10^{-3} mol dm^{-3} BTPPACl 10×10^{-3} mol dm^{-3} LiCl (aq)	10×10^{-3} mol dm^{-3} BTPPATPBCl (DCE)	dendrimer 10×10^{-3} mol dm^{-3} LiCl (aq)	AgCl	Ag

Cell I

The supporting electrolytes were 1.0×10^{-2} mol dm^{-3} lithium chloride for the aqueous phase, and 1.0×10^{-2} mol dm^{-3} bis(triphenylphosphoranylidene)ammonium terakis(4-chlorophenyl)borate (BTPPATPBCl) for the organic phases, respectively. BTPPATPBCl was prepared by metathesis of bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl) (Fluka > 98%) and potassium tetrakis(chlorophenyl)borate (Aldrich 98%). The organic solvent, 1,2-dichloroethane (DCE), was of HPLC grade (Wako Chemicals 99.7%). 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphyrinato zinc(II) tetrasodium salt ($Na_4ZnTPPC$) was purchased from Frontier Scientific/Porphyrin Products. All other reagents were of the highest grade available and used without further purification. The aqueous solutions were prepared with purified water from a Milli-Q PLUS (Millipore). The pH of the aqueous phase was controlled by adding 0.10 mol dm^{-3} HCl for pH 1, 0.050 mol dm^{-3} LiH_2PO_4/LiOH for pH 7, and 0.001 mol dm^{-3} LiOH for pH 11.

The spectroelectrochemical cell used in all measurements was analogous to one reported previously [15]. The water|DCE interface, with a geometrical area of 0.50 cm^2, was polarized by a four-electrode potentiostat (Hokuto Denko HA1010 mM1A). Platinum wires were used as counter electrodes in both aqueous and organic phases. The Luggin capillaries were provided for the reference electrodes (Ag/AgCl) in both phases. The Galvani potential difference ($\Delta_o^w\phi \equiv \phi^w - \phi^o$) was estimated by taking the formal transfer potential of tetramethylammonium as 0.160 V and of tetrapropylammonium as −0.093 V [16].

In potential modulated fluorescence (PMF) measurements, $Na_4ZnTPPC$ was added to the aqueous phase and used as a fluorescent probe for the dendrimer. The incidence of the excitation beam from an organic phase to the liquid|liquid interface was performed by a cw laser diode of 25.2 mW at 410 nm (Neoark TC20-4030S-2F-4.5) in total-internal reflection (TIR) mode [17]. The angle of incidence to the liquid|liquid interface (ψ) was set as ca. 75°. The fluorescence emitted from the interfacial region was collected perpendicularly to the interface by an optical fiber fitted to a photomultiplier tube through a monochromator (JASCO CT-10). The ac modulated fluorescence signal was analyzed by a digital lock-in amplifier (NF LI 5640). The frequency of the ac potential modulation and the potential sweep rate were 1 Hz and 5 mV s^{-1}, respectively.

3. Results and discussion

3.1. Ion-transfer voltammetry at various pHs

Cyclic voltammograms (CVs) for the G4 PAMAM dendrimer were significantly dependent on the pH conditions of the aqueous phase. Under acidic conditions, the anodic responses increased gradually at potentials more positive than 0.1 V (Fig. 2a). The pK_a of the G4 PAMAM dendrimer was reported as 9.20 (p$K_{a,2}$) for the 64-terminal amino groups in the periphery moiety and as 6.65 (p$K_{a,1}$) for the 62-tertiary amines as branch points [18]. At pH 0.9, thus, the G4 PAMAM dendrimers exist as cationic species in the aqueous phase because of the protonation of the terminal amino groups and tertiary amines. The anodic peak observed around 0.3 V was tentatively assigned as being due to the ion-transfer of the G4 PAMAM dendrimer from the aqueous to the organic phases, and the cathodic peak around 0.2 V as the back transfer from the organic to the aqueous phases. At pH 7.1, a complex anodic wave was observed around 0.4 V in the forward scan, in which a small peak was found prior to the main peak (dot mark in Fig. 2b). The cathodic wave also exhibited an irregular shape, in which the main peak at ca. 0.3 V (dot mark in Fig. 2b) was accompanied by broad cathodic responses in regions of less positive potential. Under alkaline conditions at pH 10.7, the voltammetric responses decreased completely, and the anodic peak was not clearly observed in the potential window, although the cathodic peak for a back transfer of the dendrimer from the organic phase was found to be around 0.4 V (Fig. 2c). The pH-dependent CVs demonstrate that the interfacial process is changed by the protonation of the dendrimer. The voltammetric response in Figs. 2a–b indicates the complicated interfacial mechanism consisting of ion-transfer, adsorption, and/or interfacial complex formation between the dendrimer and the organic anions. The cathodic peak current under all pH conditions, however, was almost proportional to the square root of the potential sweep rate ($v^{1/2}$) (see Fig. 2, inset), although the anodic peak at pHs 0.9 and 10.7, buried in the gradual increase of the anodic current in the higher potential region, could not be analyzed. The linear dependence of the cathodic peak current illustrates the diffusion-controlled charge transfer process from the organic to the aqueous phase at three different pHs. The anodic peak at pH 7.1 also indicates the diffusion-controlled transfer process from the aqueous to