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Time-dependent fluorescence Stokes shift and molecular-scale dynamics in alginate solutions and hydrogels

Manika Dandapat, Debabrata Mandal*

Department of Chemistry, University of Calcutta, 92, APC Road, Kolkata 700009, India

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ABSTRACT

Alginates are water-soluble polysaccharides that bind metal cations like Ca^{2+}, producing hydrogels. Here, we have determined time-dependent fluorescence Stokes shift of a guest fluorophore to elucidate molecular length-scale local dynamics within alginate-based solutions and hydrogels. We find a major bulk water-like fast response emanating from large water pools interspersed between the polysaccharide chains, together with a minor but significant slow response. The possible origin of the latter is discussed in terms of either water molecules constituting the polysaccharide hydration shells or ion distribution and diffusion around the fluorophore dipole, or microscopic structural inhomogeneity inside the alginate-based media.

1. Introduction

Alginate is a generic name for a family of polysaccharides obtained from brown algae and bacteria. These are essentially anionic linear copolymers of (1 → 4)-linked β-D-mannuronate (M) and α-L-guluronate (G) monomer residues, as depicted in Figure 1a [1–5]. These residues occur either as M-blocks of G-blocks or MG-alternating blocks along the polysaccharide chain. The anionic alginate has an intrinsic electrostatic affinity toward certain cations, which results in strong ion-binding and extensive physical cross-linking of the polysaccharide chains in aqueous medium, eventually leading to the formation of hydrogels. Such ionotropic gelation of alginates has been reported with many metal cations like Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, etc. [6–14]. Of these, the Ca^{2+}-alginate gel has received the major share of attention primarily due to its excellent biocompatibility [6–10], high water content and soft, porous structure, which makes it eminently suitable for biomedical applications [15,16]. In fact, Ca^{2+}-alginate hydrogels are commonly used in various purposes like wound dressing [17], slow drug release systems [18–20], regenerative medicine [21], and tissue engineering [22,23].

Among the divalent alkaline earth metal ions, Ca^{2+} is found to bind with the G- and MG-blocks, $Ba^{2+}$with G- and M-blocks while Sr^{2+}binds only with the G-blocks [9]. Gelation of alginates at $[Ca^{2+}]$: [G-residue] > 0.25 is generally described by the egg-box hypothesis [6,7,24–26] as depicted in Figures 1b and 2: G-blocks along the polymer chain adopt a 2/1 helical conformation, creating buckled zones, with the Ca^{2+} ions coordinated within the cavities enclosed by a pair of buckled G-blocks. Subsequently, at $[Ca^{2+}]$: [G-residue] > 0.55, experimental data indicates the emergence of multimers due to lateral association of egg-box dimers, as illustrated in Figure 2 for both short-chain and long-chain alginates [26].

Alginate based gels have been extensively studied using techniques like X-ray diffraction, calorimetry, viscometry and rheological measurements [24–29]. These studies have helped to construct a fairly comprehensive picture of the microscopic structure inside the gels comprising of anionic polysaccharide chains encompassing water-filled pools. However, an equally important problem remains largely un-addressed: the dynamics operating in these length-scales. For example, neutron scattering experiments done by Tripadus et al. [30] have revealed the diffusive motion of water molecules confined inside the water-pools. Very recently, Mazur et al. [31] have performed dielectric spectroscopy and fs-IR spectroscopy on aqueous alginate solutions. They demonstrated that, in spite of the very high macroscopic viscosity of the solutions, rotational dynamics of the water molecules within the solutions was remarkably fast, similar to that observed in bulk water. Only a minute fraction of water molecules belonging to the first hydration shell of the polysaccharide chains and Na^+ counterions exhibit markedly slow mobility. In other words, the overwhelming majority of water molecules in these solutions actually reside in sufficiently large water-pools where bulk-like conditions prevail. Apart from water, the long anionic polysaccharide chains, together with the large number of cationic counterions accompanying them,

* Corresponding author.
E-mail address: dmandal.chemistry@gmail.com (D. Mandal).

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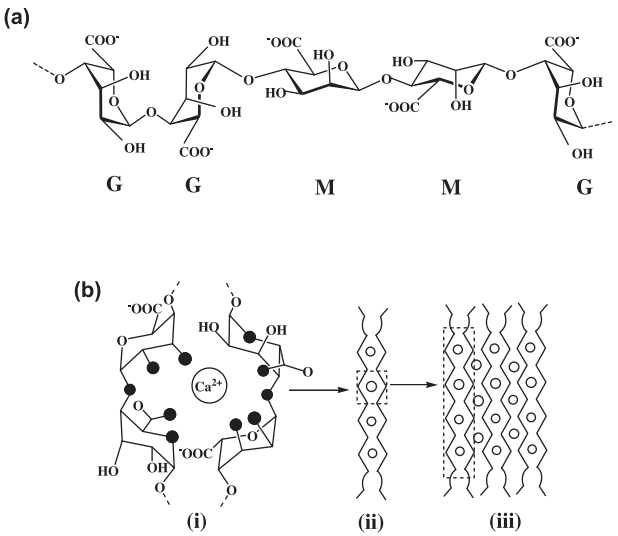

Figure 1. (a) Structure of alginate:β-D-mannuronate (M) and α-L-guluronate (G) monomer residues along alginate polymer chain. (b) Schematic representation of egg-box junction zones in alginate/Ca^{2+} gels, as proposed by Grant et al. (Ref. [6], 24–26): coordination of Ca^{2+} in a cavity created by a pair of guluronate sequences along alginate chains (i); egg-box dimer (ii), and laterally associated egg-box multimer (iii). The black solid circles represent the oxygen atoms and open circles represent Ca^{2+} ions.

may also profoundly contribute to the dynamics. In this context, we refer to an analogous family of compounds – the ionic liquids. Ionic liquids are low-melting organic salts consisting of long alkyl chain-bearing cations and their counter-anions. Extensive experimental and computational studies on ionic liquids have indicated that factors like microscopic structural inhomogeneity and ionic diffusion play a major role in deciding the nature of their molecular-scale dynamics [32–41]. A similar possibility exists for the alginate solutions and hydrogels.

The question then arises as to how a small guest molecule inserted in an alginate solution or hydrogel, would report on this molecular-scale dynamics occurring in its immediate vicinity within the host medium. We were especially interested to see if the dynamics differed between solution and hydrogel, and at different concentrations of the added cross-linking metal cation. For this purpose, we selected the fluorophore Coumarin 102 (C102, also called Coumarin 480), well-known as a solvation dynamics probe for bulk water as well as for water entrapped in supramolecular organized assemblies [42–44]. C102 is a flat, rigid molecule with a large difference in ground and excited state dipole moments: $|\boldsymbol{\mu}_e - \boldsymbol{\mu}_g|$. In a polar solvent like water, the solvent molecular dipoles arrange themselves around the ground-state fluorophore in a configuration that maximizes favorable dipole–dipole interactions. When the fluorophore is excited with an ultrashort light pulse, its dipole moment changes rapidly from $\boldsymbol{\mu}_g$ to $\boldsymbol{\mu}_e$. The surrounding polar solvent molecules respond to this sharp change by slowly reorienting themselves around the excited state fluorophore dipole. In other words, these solvent molecules undergo relaxation into a new stable configuration. The rate of this solvent relaxation, which can be estimated from the time-dependent fluorescence Stokes shift of the fluorophore emission, reflects the molecular-scale dynamics in the local solvent environment of the fluorophore [42]. Solvent relaxation in pure, bulk water occurs in <1 ps time-scales [45,46], while in water confined in organized assembles, it is remarkably slowed down to ~1 ns [42–44].

At this point, we emphasize that solvent dipolar reorientation is by no means the only mechanism for solvation dynamics. Solvation dynamics using similar coumarin fluorophores have been highly well-documented even in ionic liquids, which are completely devoid of dipolar solvent molecules like water. Here, solvent dipolar realignment around the excited solute dipole $\boldsymbol{\mu}_e$ is absolutely inconceivable. Nevertheless, these solvents do display solvation dynamics extending from sub-picoseconds to nanoseconds [32–35]. Computer simulations indicate that this wide range of time-constants actually reflects the reorganization of ions around the solute dipole over diverse length- and time-scales [36,37]. The ultrafast initial response is due to ions localized in the first solvation shell of the solute [36], while reorganization of distant ions is strongly coupled with the thermal motions in the solvents, and are much slower [33,38]. In fact, the slower, nanosecond dynamics largely involves translational motion of these ions [32,39]. Moreover, the integral solvation times in ionic liquids correlate remarkably well with their macroscopic conductivity, highlighting the close relationship between ion-transport and solute dipole stabilization [32]. Another important factor contributing

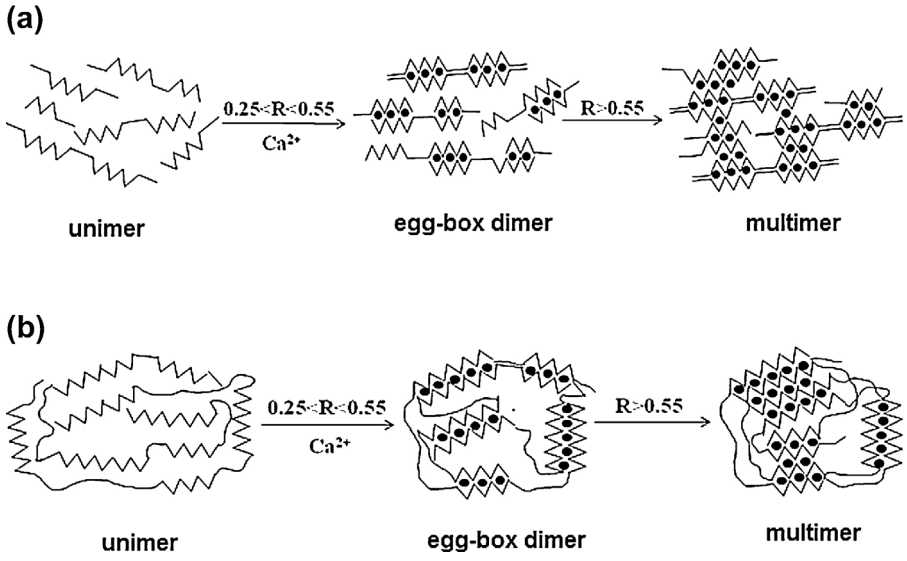

Figure 2. Schematic representation of binding of Ca^{2+} to (a) short-chain and (b) long-chain alginates, showing the different forms of alginate (unimer, egg-box dimer and associate multimer) that emerge at different regimes of $R = [Ca^{2+}]/[\text{G-residue}]$, according to Fang et al. (Ref. [26]). The zigzag lines, smooth lines, and dots stand for G blocks, M blocks and Ca^{2+} ions, respectively.