New insights into viscosity abnormality of sodium alginate aqueous solution[☆]

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ARTICLE INFO

ABSTRACT

The viscosities of dilute sodium alginate aqueous solutions have been measured at various temperatures. The upward bending phenomenon of the reduced viscosity of sodium alginate solution in the dilute concentration region resulted from the adsorption of polymer on the glass capillary wall. Experimental viscosity data satisfactorily coincided with the recent theory regarding the adsorption effect of polyelectrolyte. The theory predicted that the second term of reduced viscosity would vanish due to the presence of inter-chain Coulombic repulsion interaction, which prevents self-association or cluster formation in the experimental concentration regime. Furthermore, temperature dependence of the hydrodynamic diffusion constants of sodium alginate in aqueous solution was measured by dynamic light scattering (DLS). The morphologies of sodium alginate on the glass surface were also investigated by atomic force microscope (AFM). A self-consistent result was obtained quantitatively by different experimental means.

1. Introduction

Polyelectrolyte is a type of polymer with positive or negative charges on its repeating units. It dissociates in solution, forming a charged polyion surrounded by an atmosphere of small, mobile counterions. Since many important biological macromolecules are polyelectrolytes, such as DNA and RNA, significant attention has recently been focused on this type of polymer. Furthermore, many synthetic polyelectrolytes have important technological applications (Flory, 1953; Holm, Rehahn, Oppermann, & Ballauff, 2004; Radeva, 2001; Thunemann, 2002).

Generally, polyelectrolyte behavior can be described by the effects arising from intra-chain electrostatic forces between charges presented on the chain backbone. For example, the famous phenomenon of upward bending of reduced viscosity versus the concentration plot of polyelectrolyte solution in the dilute concentration region is ascribed to the intra-chain electrostatic repulsion of charges on the same backbone. This leads to chain extension and an increase of reduced viscosity upon dilution (Flory, 1953; Fuoss & Sstrauss, 1948; Radeva, 2001). The upward bending phenomenon of viscosity has therefore been regarded as a typical nature of polyelectrolyte. In literature, it is defined as the "polyelectrolyte effect."

The solution viscosity in a dilute solution is made complicated by the adsorption of the polymer on the capillary wall, which influences the determination of solution viscosity (Boyer & Streeter, 1955; Ohrn, 1955; Ohrn, 1956; Ohrn, 1958; Streeter & Boyer, 1954). Recently, Cheng et al. (Cheng, 1997; Cheng, Shao, Liu, & Qian, 1998; Cheng, Yang, & Yan, 1999) put forward a quantitative treatment of the effect of polymer adsorption on the capillary viscometry of polymer solutions. They obtained a correction formula for the relative viscosity of a polymer solution:

$$\eta_{r,\exp} = \eta_{r,\text{true}} \cdot \left[1 + \frac{k \cdot C}{C_a + C}\right] \qquad (1)$$

where $\eta_{r,\exp}$ and $\eta_{r,\text{true}}$ are the experimental viscosity and true relative viscosity, respectively; k is a parameter related to the adsorption layer thickness; and C_a is the concentration at which half the active sites of the viscometer wall are adsorbed by the polymers. The parameters k and C_a could be experimentally evaluated. This correction formula is also applicable to slip flowing liquids, where k becomes negative and C_a vanishes (Cheng, 1997; Cheng et al., 1998; Cheng et al., 1999). True relative and specific viscosities of polymer solution can be expressed as

$$\eta_{r,\text{true}} = 1 + [\eta] \cdot C + 6 \cdot K_M \cdot [\eta] \cdot C^2 \qquad (2)$$

and

$$\frac{\eta_{sp}}{C} = [\eta] + 6 \cdot K_M \cdot [\eta] \cdot C \qquad (3)$$

where K_M is the molar self-association constant resulting from either inter-chain cohesion or cluster formation (Pan & Cheng,

2000). The slope constant K_M in Eqs. (2) and (3) simply correlates with the conventional dimensionless Huggins constant K_H as

$$K_M = \frac{K_H \cdot [\eta]}{6} \tag{4}$$

and is numerically interchangeable.

However, the physical meanings of these two parameters are quite different. The Huggins slope constant is dimensionless, while the molar self-association constant reveals the tendency of inter-chain cohesion due to chain penetration in solution, by which the dynamic contact concentration proposed by Qian (2002) could be evaluated. The theory was derived from the assumption that the viscosity of polymer solution before chain overlapping should obey Einstein law. Any deviation from this ideal situation would have been caused by cluster formation due to inter-chain cohesive self-association. A polyelectrolyte molecule has a charge on each repeating unit, and the strong Coulombic repulsion interaction prevents inter-chain cohesion and cluster formation. Hence, for the polyelectrolyte, the molar self-association constant K_M is essentially equal to zero. The experimental relative viscosity of its solution can be deduced from Eq. (1) to derive the following formulation:

$$\eta_{r,\exp} = [1 + [\eta] \cdot C] \cdot \left[1 + \frac{k \cdot C}{C_a + C}\right] \tag{5}$$

The validity of Eq. (5) has been confirmed for a number of cases, including proteins (Li & Cheng, 2006; Li, Cai, Zhong, & Cheng, 2008).

Recently, Cai, Dai, Yang, and Cheng (2009) studied the viscosity behavior of chitosan in 1% acetic acid solution. Generally, chitosan dissolves only in acidic media, through which it is converted to cationic polyelectrolyte because of the protonization of the –NH$_2$ group on the C-2 position of the D-glucosamine repeat unit (Rinaudo, 2006). However, based on experimental facts, the reverse viscosity behavior, that is, downward bending phenomenon of the curves of reduced viscosity of chitosan versus the concentration in dilute solution region, has been observed. Possible reasons for this are the presence of excess acetic acid and the similarity of the solution properties of chitosan to those of neutral polymers, rather than to those of polyelectrolytes (Cai et al., 2009). Compared with chitosan, sodium alginate is a kind of polyelectrolyte with strong negative charges on its backbone. It could dissolve well in pure water without any additives. Sodium alginate is a linear, binary copolymer of $(1 \rightarrow 4)$ linked β-D-mannuronate (M) and α-L-guluronate (G) residues arranged in a non-regular, block-wise fashion along the chain. It is also a biopolymer that has been widely studied and applied in various fields (Moe, Draget, Skjak-Braek, & Smidsrod, 1995; Wang, Zhang, Konno, & Saito, 1994; Yang, Chen, & Fang, 2009; Zhang, 2006; Zhang, Wang, Wang, Guo, & Zhang, 2001). However, previous studies related to the viscosity properties of alginate aqueous solutions all ascribed to the conventional "polyelectrolyte effect."

In the present work, the viscosities of sodium alginate aqueous solutions at different temperatures have been measured and analyzed based on the new theory cited above. The adsorbed polyelectrolyte layer on the capillary wall formed an ionizable brush repulsive to the flowing solution in the capillary. For the investigation of correlations between the brush and the flowing polyelectrolyte solution, the morphologies of sodium alginate on a glass surface and its hydrodynamic diffusion constant were measured by atomic force microscope (AFM) and dynamic light scattering (DLS), respectively.

2. Experimental

2.1. Materials

The sodium alginate sample was a commercial product purchased from China Pharmaceutical Co., the source of which was Macrocystis Pyrifera. It was purified further before measurements with the reported method (Yuan & Chen, 2002). Sodium alginate was analyzed by ^{1}H NMR spectroscopy using a Bruker DRX-500 (500 MHz) spectrometer. The M/G ratio was estimated to be 1.75 (Grasdalen, 1983; Grasdalen, Larsen, & Smidsrod, 1979). Viscosity average molecular weight, $M_\eta = 6.5 \times 10^4$ g/mol, was estimated from the intrinsic viscosity determined in the 0.1 M NaCl solvent using the Mark-Houwink parameters: $\alpha = 1.13$, $K = 6.9 \times 10^{-4}$ ml/g at 25 °C (Martinsen, Skjak-Brak, Smidsrod, Zanetti, & Paoletti, 1991).
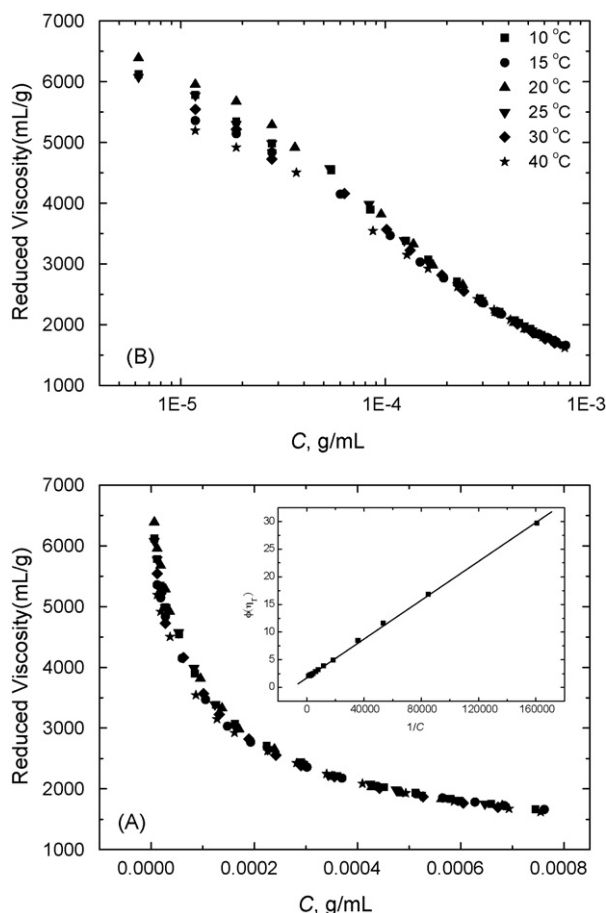
2.2. Viscosity measurement

A stock solution of the sodium alginate was freshly prepared at room temperature. De-ionized water was used in all experiments. Viscosity measurements were carried out using an Ubbelohde-type capillary viscometer 0.40 mm in diameter and 10.0 cm in length. The measured temperature from 10 °C to 40 °C (±0.01 °C) was controlled by a circulating water bath. A known weight of solvent (de-ionized water) was transferred into the viscometer, and its efflux time t_v was measured carefully. Then, a definite amount of stock sample solution with known weight concentration was added into the viscometer by successive weighing until the relative viscosity reached a predetermined point. This was performed to increase the solution concentration in the viscometer. The efflux time t_u for each solution with different concentrations in the viscometer was measured. The ratio of flow time of solution to that of solvents, t_u/t_v, was regarded as the relative viscosity.

2.3. Dynamic light scattering (DLS)

Hydrodynamic radius R_h of the sodium alginate in de-ionized water with a concentration of 0.05% was determined by the DLS model of Brookheaven BI200SM at varied temperatures. Uniphase He-Ne laser ($\lambda_o = 532$ nm) was used as the light source. Scattering angle was 90°. All analyses based on the CONTIN procedure were performed, with each run lasting for 3 min. For a diffusion relaxation, Γ is related to the translation diffusion coefficient D by $(\Gamma/q^2)_{c \to 0, q \to 0} \to D$, so that the R_h can be calculated via Stokes–Einstein equation, $R_h = (k_\beta T/6\pi\eta)D^{-1}$, where k_β, T and η are the Boltzmann constant, the absolute temperature and the solvent viscosity, respectively. The final results were the average of three runs.

2.4. Atomic force microscope (AFM)

Atomic force microscope (CSPM, Guangzhou Benyuan Co., China) was used to study the different morphologies of adsorbed sodium alginate on the glass slides treated by sodium alginate solution. The detailed process for the treatment of glass slides consists of the following steps: a clean slide with glass quality similar to that of the capillary viscometer was vertically dipped repeatedly in sodium alginate solution with a concentration of 0.05%, which simulated the viscous flow of polymer solutions in the capillary. Next, the treated glass slide was washed with de-ionized water and dried under nitrogen atmosphere at 80 °C for further AFM observation. A clean glass slide without any treatment was taken as a reference. AFM measurement was performed with a 20-mm scanner in tapping mode.

Fig. 2. Temperature dependence of the viscosity parameters $[\eta]$ and b_{eff} obtained by fitting the data with Eq. (5).

Fig. 1. The plot of reduced viscosity of sodium alginate aqueous solutions versus concentration (A) and logarithmic concentration (B) at various temperatures. The straight line inserted in the corner of (A) is the plot of function $\Phi[\eta]$ versus $1/C$ for the viscosity measured at 10 °C.

3. Results and discussion

The concentration dependence of measured reduced viscosities of sodium alginate aqueous solutions at varied temperatures is shown in Fig. 1A. At a glance, the reduced viscosities of sodium alginate bent upward upon dilution independently from temperature. This is considered a typical "polyelectrolyte effect" in view of the traditional idea. However, if the concentration was expressed in logarithmic scale, as shown in the top part of Fig. 1B, the viscosities were actually temperature-dependent, possibly because of different dynamic motion of polymer chains in solutions of various temperatures.
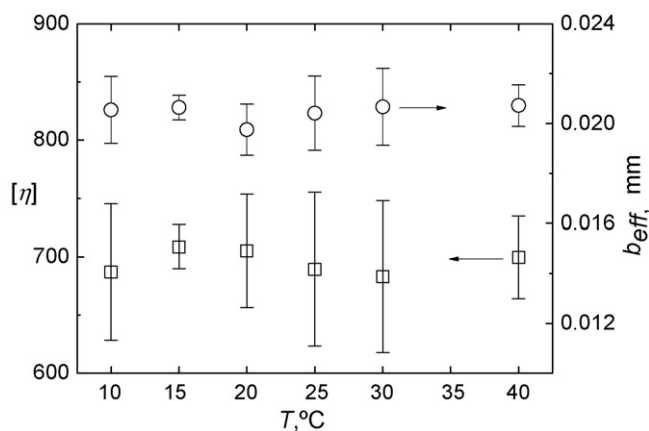
However, based on the adsorption theory cited above, the solute adsorption reduced the radius of the capillary of the viscometer, while the actual concentration of the solution decreased at the same time. Two opposite effects affected the viscosity measurement. If the former effect was much more marked than the latter, then the reduced viscosity was bending upward. According to the adsorption theory mentioned above, Eq. (5) may thus be rewritten as

$$\frac{1 + [\eta] \cdot C}{\eta_{r,\exp} - [1 + [\eta] \cdot C]} = \frac{1}{k} + \frac{C_a}{k} \cdot \frac{1}{C} \tag{5a}$$

To define a viscosity function

$$\Phi = \frac{1 + [\eta] \cdot C}{\eta_{r,\exp} - [1 + [\eta] \cdot C]} \tag{6}$$

Based on this, the plot of Φ versus $1/C$ would be linear. The viscosity parameters $[\eta]$, k, and C_a could be evaluated directly using the

nonlinear curve fitting technique or by the function Φ in order to search for the best straight line for the Φ versus $1/C$ plot with a maximum linear correlation coefficient. The results of the two methods were fully identical. An example of Φ versus $1/C$ plot for $T = 10$ °C was inserted in the right corner of Fig. 1A. For other samples at different temperatures, the Φ versus $1/C$ plots gave slightly different intercepts and slopes by which the three viscosity parameters were evaluated, respectively.

Based on the simulated results, in the 10–40 °C temperature range, intrinsic viscosity varied sinuously only within a limited range of 682–708 ml/g as shown in Fig. 2. It is well known that $[\eta]$ reflects the hydrodynamic volume of polymer single chain in an extremely dilute solution, and sodium alginate is a strong anionic polyelectrolyte, the stiffness conformation of which has little change for strong intra-molecular electrostatic repulsion. Thus, $[\eta]$ almost showed temperature independence in the measured temperature range.

Furthermore, effective thickness of the adsorbed layer (b_{eff}) could be evaluated from the parameter k coupled with the known capillary radius as R (Cheng et al., 1999). The R of the capillary of the viscometer was determined to be 0.40 mm.

$$b_{eff} = R \cdot \left[1 - \frac{1}{(1 + k)^{1/4}} \right] \tag{7}$$

Using the equation above, the effective adsorption thickness b_{eff} of sodium alginate on the capillary wall was deduced from k. The result is plotted in Fig. 2. The mean value of b_{eff} was 0.0205 mm. This effective thickness included a repulsion layer between the swollen adsorbed brush on capillary surface and the flowing polyelectrolyte solution in the capillary.

The hydrodynamic radius R_h of the sodium alginate aqueous solution has been measured in the same temperature interval by DLS. In addition to R_h, the radius of gyration R_g of the alginate samples were estimated primarily from its hydrodynamic volume by

$$V_h = \frac{4}{3} \cdot \pi \cdot \left\langle R_g \right\rangle^3 \tag{8}$$

where

$$V_h = [\eta] \cdot M \tag{9}$$

according to Smidsrod and Haug (1968).

The temperature dependence of both R_g and R_h are plotted in Fig. 3A. The R_g was nearly constant, while R_h was smaller than R_g and decreased with increasing temperature. R_h was related to the translation diffusion of polymer, which also accompanied the motion of adjacent solvent molecules in the same direction. R_h
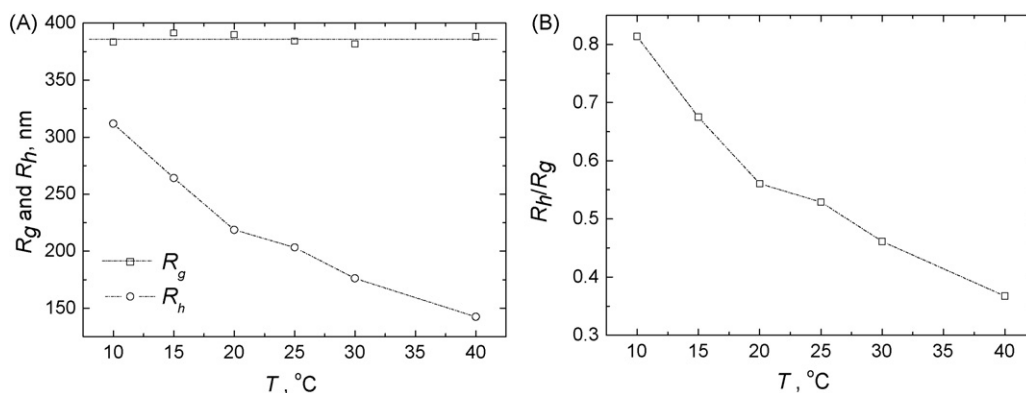
Fig. 3. Temperature variations of the R_g, R_h (A), and the ratio R_h/R_g (B).
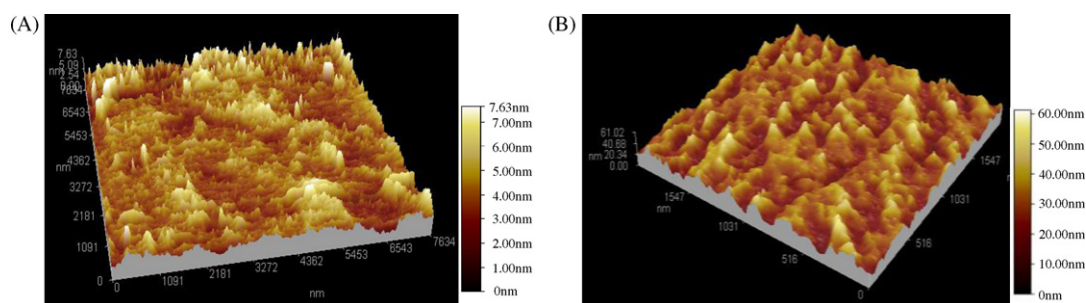

Fig. 4. AFM images of a clean glass surface (A) and a glass surface with a layer of adsorbed sodium alginate in the dry state (B).

could be deduced from Stokes–Einstein equation. With the temperature increase, the Brownian motion of the polymers was more active, and the translation diffusion coefficient increased, which resulted in the decrease of R_h.

Furthermore, the ratio R_h/R_g decreased from 0.81 at 10 °C regularly to 0.36 at 40 °C, as shown in Fig. 3B. This fact demonstrated the effect of temperature on the translation diffusion of alginates in solution. Since the viscosity data indicated that the alginates possessed an extended conformation, the decrease of the solvation effect of the polymer chains with temperature increase caused the alginate chain to move faster.

A direct observation of the glass surface with and without adsorption of sodium alginate has been measured by AFM. A clean slide having similar glass quality was used, and the action of viscous flow of polymer solutions in the capillary was simulated. The glass slide was vertically dipped into the sodium alginate aqueous solution repeatedly. It was then fully washed with de-ionized water and dried further before AFM measurement. The same treatment was applied to a blank slide as reference.

The surface roughness of the blank glass slide is clearly shown in Fig. 4A. Values varied from 0 to 7.63 nm. From Fig. 4B, the sodium alginate molecules were firmly adsorbed on the glass surface and could not be removed by repeated washing with water. The thickness of the adsorbed layer of sodium alginate varied within the range of 0–60 nm. After subtracting the blank, the average thickness of adsorbed sodium alginate in the dry state was near 40 nm on the slide. However, based on previous calculations, the average thickness of b_{eff} was 0.0205 mm, much larger than 40 nm. One reason is that the thickness observed directly under AFM was measured in the dry state, a condition far different from the swollen state. Another reason is that the effective thickness of the adsorbed layer (b_{eff}) comprised the swollen adsorbed solute layer (b_{ads}) and the electrostatic exclusion layer (b_e). Therefore, if single-molecular layer adsorption for sodium alginate was assumed on the capillary surface, b_{ads} could be estimated as primarily equal to $2R_g$ near

770 nm. It was deduced further that b_e was almost 25 times thicker than b_{ads}.

However, although the thickness of sodium alginate on the glass slide observed by AFM was smaller than that of chitosan, which might be due to the different molecular weights of the two samples, the calculated b_{eff} of sodium alginate was one order of magnitude larger than that of chitosan (Cai et al., 2009). The electrostatic exclusion layer in chitosan system has been eliminated effectively by excessive acetic acid for the charge screening effect. This resulted in the large decrease of b_{eff} of chitosan.

4. Conclusion

The problem of viscosity abnormality of polyelectrolyte solution has been explained based on the theory of solute adsorption and self-association upon viscometry of polymer in solution. The conventional "polyelectrolyte effect" was the result of adsorption of the polyelectrolyte on the capillary wall surface. This adsorption effect of polyelectrolyte could be expressed quantitatively in a simple equation by which the intrinsic viscosity and two parameters related to effective adsorption layer thickness, and the concentration which half the active sites of the wall surface occupied, could be evaluated. Temperature dependence of the radius of gyration from the viscosity data and hydrodynamic radius from DLS demonstrated the effect of chain stiffness. The existence of this adsorption layer for sodium alginate was confirmed by direct AFM observation.

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