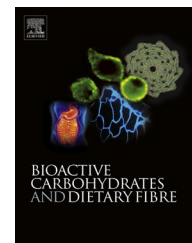


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Interactions between schizophyllan and curdlan molecules in solutions

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ABSTRACT

The polymer–polymer mutual interactions of two structurally similar and bioactive polysaccharides, schizophyllan (SPG) and curdlan (CUD) were investigated by means of intrinsic viscosity measurements. A weak repulsion exists between SPG and CUD molecules in dimethylsulfoxide (DMSO) solutions, which might be attributed to the presence of glucosyl side groups on SPG backbone. On the contrary, in 0.25 M aqueous sodium hydroxide (NaOH) solutions, a relatively strong attractive interaction is present and leads to the intermolecular aggregation of SPG and CUD.

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1. Introduction

Studies of mutual interactions between two different types of macromolecules are of both theoretical and industrial importance. For instance, the clarification of polymer–polymer interactions allows the prediction of the miscibility of polymer blends (Chee, 1990; Kuleznev, Melnikova, & Klykova, 1978; Kundu, Ray, Adhikari, & Maiti, 1986). In the field of biopolymer science, numerous attempts have been made to investigate the synergistic interactions between polysaccharides, which are considered to play an important role in the formation of mixed gels (Annable, Williams, & Nishinari, 1994; Cairns, Atkins, Miles, & Morris, 1991; Cairns, Miles, & Morris, 1988; Goycoolea, Richardson, Morris, & Gidley, 1995;

Kohyama, Iida, & Nishinari, 1993; Kohyama, Sano, & Nishinari, 1996; Miyoshi, Takaya, Williams, & Nishinari, 1996; Nishinari, Miyoshi, Takaya, & Williams, 1996; Ridout, Brownsey, & Morris (1998); Ridout, Cairns, Brownsey, & Morris, 1998; Ross-Murphy, Shatwell, Sutherland, & Dea, 1996; Williams, Clegg, Langdon, Nishinari, & Piculell, 1993; Yoshimura, Takaya, & Nishinari, 1996).

Various methods have been employed to study macromolecular mutual interactions, including light scattering, viscometry, differential scanning calorimetry, Fourier transformation infrared spectroscopy, etc. Among these, viscometry is a simple and useful method since it requires no expensive and precious equipment but offers an effective approach to understand how macromolecules behave and interact in solutions (Morris, 1984; Morris, Rees, Robinson, &

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Young, 1980; Staszewska, Kovar, & Bohdanecky, 1980; Sun, Wang, & Feng, 1992; Vasile & Schneide, 1971; Wang, Sun, & Wang, 2001). Morris et al. proposed a method to analyze the interactions between two polysaccharides, in which the solutions of two polysaccharides were prepared separately and adjusted to give an identical viscosity, and then they were mixed in varying proportions (Morris et al. 1980; Morris, 1984). If the measured viscosities of mixed solutions are considerably higher than those of unmixed solutions, it implies that a strong synergistic interaction exists between the two polysaccharides. In parallel, the opposite situation suggests the presence of strong antagonistic interaction. Furthermore, if the viscosities of mixed solutions are equal to those of unmixed solutions at various proportions, it means that there is no strong specific interaction between the two polysaccharides. It should be pointed out that this situation only indicates the absence of strong specific interactions, which in no way excludes the possibility of the existence of other weak thermodynamic interactions. A more accurate analysis is necessary, and can be accomplished by examining the Huggins constants of mixed solutions at various compositions (Cragg & Bigelow, 1955; Krigbaum & Wall, 1950; Sun et al., 1992). The Huggins constants can be obtained from intrinsic viscosity measurements. The classical Huggins equation expresses the specific viscosity η_{sp} of a polymer as a function of polymer concentration c in the following form:

$$\frac{\eta_{sp}}{c} = [\eta] + k_1[\eta]^2 c \quad (1)$$

where $[\eta]$ and k_1 are the intrinsic viscosity and the Huggins constant, respectively. In practice, the Huggins equation is always combined with the following Kraemer equation, a derivative from the Huggins equation, to determine $[\eta]$:

$$\frac{L\eta_r}{c} = [\eta] - k_2[\eta]^2 c \quad (2)$$

where η_r is the relative viscosity ($\eta_r = \eta_{sp} + 1$), and k_2 is the Kraemer constant. Both the Huggins constant and Kraemer constant are important parameters, which to some extent reflect the conformation and solubility of polymer chains in solutions.

For a ternary (polymer-A)-(polymer-B)-solvent system, three types of polymer-polymer interactions might contribute to the value of Huggins constant k_1 (Cragg & Bigelow, 1955; Sun et al., 1992), these are

- (1) Long-range hydrodynamic interaction of pairs of single molecules, which exists in the forms of A-A, B-B and A-B in a ternary system:

$$k_{hydro} = \frac{k_a[\eta]_a^2 W_a^2 + k_b[\eta]_b^2 W_b^2 + 2\sqrt{k_a k_b} [\eta]_a [\eta]_b W_a W_b}{([\eta]_a W_a + [\eta]_b W_b)^2} \quad (3)$$

where k_a , k_b , $[\eta]_a$, and $[\eta]_b$ are the Huggins constants and intrinsic viscosities of polymer-A and polymer-B, respectively. W_a and W_b are the weight fraction of polymer-A and polymer-B.

- (2) Formation of double molecules due to aggregation. It is worthy of noting that even the double molecules whose

existence is instantaneous can contribute to this term:

$$k_{aggre} = \frac{P}{[\eta]^2} ([\eta]_{(2)} - [\eta]_{(1)}) \quad (4)$$

where $[\eta]_{(2)}$ and $[\eta]_{(1)}$ are the intrinsic viscosities of the double and single molecule species, respectively, and P is a constant. In the absence of strong specific interaction that leads to aggregation and at sufficiently low concentration, this term is negligible.

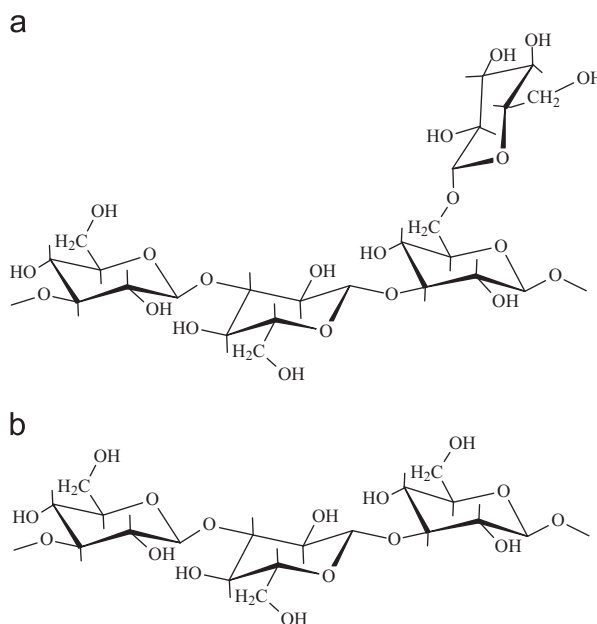
- (3) Intermolecular attraction or repulsion, k_{thermo} ; $k_{thermo} > 0$ suggests attraction, while $k_{thermo} < 0$ suggests repulsion.

Hence, $k_1 = k_{hydro} + k_{aggre} + k_{thermo}$. In the absence of strong specific interactions, it reduces to the following form:

$$k_{thermo} = k_1 - k_{hydro} \quad (5)$$

It is easily concluded that, if $k_1 > k_{hydro}$, there exists an attraction between polymer-A and polymer-B, while $k_1 < k_{hydro}$ indicates the presence of a repulsion between polymer-A and polymer-B. Accordingly, we can study the interactions of two different kinds of macromolecules more precisely by virtue of Eq. (5).

Schizophyllan (SPG) is a neutral extracellular polysaccharide produced by the fungus *Schizophyllum commune*. Its chemical structure is composed of linearly linked β -(1 \rightarrow 3)-D-glucose residues with one β -(1 \rightarrow 6)-D-glucose side group for every three main chain residues (Kikumoto, Miyajima, Kimura, Okubo, & Komatsu, 1971) (Scheme 1a). The backbone structure of SPG is exactly identical to that of curdlan (CUD). However, CUD carries no side group (Scheme 1b). Due to the antitumor activities arising from their triple helical conformations, both SPG and CUD have been attracting more and more attention (Gao et al., 1997, 1998; Yoshioka, Uehara, & Saito, 1992). Additionally, because of its unique gelling ability, CUD has been the subject of numerous investigations in the area of food science



Scheme 1 – Repeating units of schizophyllan (a) and curdlan (b).

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