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Viscosity and Solubility Behavior of the Polysaccharide Inulin in Water, Water + Dimethyl Sulfoxide, and Water + Isopropanol Media

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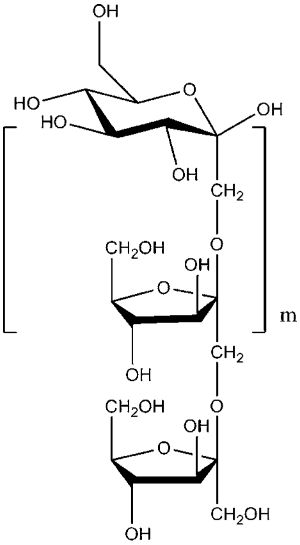
Inulin, the β (2→1) fructosyl fructose unit-containing polysaccharide, exhibits interesting solution properties. In this study, viscosity and solubility behaviors of the polysaccharide have been examined in water, water + dimethyl sulfoxide (DMSO), and water + isopropanol (IP) media. The compact (globular) molecular configuration of the biopolymer in aqueous medium becomes nonspherical and elongated in both water + DMSO and water + IP with an increasing proportion of the nonaqueous solvents in the media. The solubility of inulin is a weak endothermic process in an aqueous medium which in the presence of IP in water becomes progressively exothermic by way of favorable molecular aggregation. The solubility decreases by the presence of IP in the mixed solvent medium.

Introduction

The biopolymer inulin, a β (2→1) fructosyl fructose unit containing polydisperse polysaccharide (Scheme 1), has many uses and applications.[1−6] It is a favorable diabetic food ingredient, a fat replacer, and a colon and mammary tumor inhibitor. It can increase absorption of both calcium and magnesium as well as promote the growth of intestinal bacteria. It can be directly converted to ethanol, thus having a potential for converting crops with high inulin content to fuel. It occurs in plants as a reserve polysaccharide,[7,8] and the most important sources are *Cichorium intybus* (chicory), *Dahlia pinuata cav.* (dahlia), and *Helianthus tuberous* (Jerusalem artichoke). It can be synthesized in vitro.[9,10] Electron diffraction patterns and X-ray powder diffraction studies have revealed orthorhombic[11] and pseudohexagonal[12] geometry for the hydrated (one molecule of water per fructosyl unit) and semihydrated (half a molecule of water per fructosyl unit) inulin, respectively. A literature survey reveals that although the biopolymer has been characterized in the solid state as well as in solution, such studies are limited.[13,14] The determination of the molar mass and viscosity of the polymer in water and dimethyl sulfoxide (DMSO) has been studied earlier.[15] In a recent study,[16] the solubility and viscosity behavior of inulin in an aqueous medium have been presented. However, the general solution properties of the compound have not been adequately explored in the past. This is required for the proper and appropriate uses and applications of the polymer in the chemical, pharmaceutical, and medicinal fields. In a recent publication,[17] we have presented the characterization of inulin (isolated from chicory) with reference to its molar mass, hydration in solution, and sorption of water vapor by the solid mass as well as its configuration in solution adopting different physical methods. The biopolymer has been found to become moderately hydrated and to absorb water vapor, and it forms spheroidal and rod-like molecular aggregates in water and water + DMSO, respectively. It has produced characteristic intrinsic viscosity values in the above-mentioned solvents.

Scheme 1. Structure of Inulin



The above findings on the polysaccharide inulin has prompted us to investigate in detail its solution properties with reference to viscosity and solubility in water, water + DMSO, and water + IP (isopropanol) media. The results have been comprehensively presented and physicochemically analyzed.

Experimental Section

Materials. The inulin, *D*-Fruf-(2→1)-(*D*-Fruf)$_{35x}$-(2→3)-*D*-G$_p$-(1→1)-(*D*-Fruf)$_x$-(2→1)-*D*-G$_p$ (a polysaccharide extracted from chicory), used was a 99 % pure product of Sigma (USA) of 4450 (by light scattering) weight average molar mass used by us in an earlier work.[17] Analytical reagent grade DMSO and IP were obtained from Merck (Germany) and SRL (India), respectively. The chemicals were used as received. The desiccated inulin was used in all experiments. The concentration of inulin used has been expressed in weight percent throughout the text. Doubly distilled water (specific conductance, $\kappa = (2$ to $3)\ \mu\text{s}\cdot\text{cm}^{-1}$ at 303 K) was used for preparation of all solutions.

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Table 1. Viscosity (η) and Reduced Viscosity (η_{sp}/C) of Inulin Solution in the Water (1) + DMSO (2) Medium at 303 K

100 x_2	C / kg·L^{-1}	η / mPa·s	η_{sp}/C / L·kg^{-1}	C / kg·L^{-1}	η / mPa·s	η_{sp}/C / L·kg^{-1}
0	0.002	0.805	0.049	0.008	0.829	0.051
	0.004	0.813	0.050	0.01	0.838	0.052
	0.006	0.821	0.051	0.012	0.847	0.053
25	0.002	2.722	0.059	0.008	2.834	0.065
	0.004	2.759	0.062	0.01	2.873	0.067
	0.006	2.796	0.064	0.012	2.915	0.069
33.33	0.002	3.056	0.066	0.008	3.188	0.076
	0.004	3.099	0.069	0.01	3.236	0.079
	0.006	3.148	0.073	0.012	3.282	0.082
50.0	0.002	2.811	0.080	0.008	2.945	0.086
	0.004	2.847	0.083	0.01	2.997	0.087
	0.006	2.896	0.085	0.012	3.067	0.089
66.7	0.002	2.319	0.112	0.008	2.486	0.120
	0.004	2.373	0.115	0.01	2.547	0.123
	0.006	2.428	0.118	0.012	2.60	0.126
85.7	0.002	1.967	0.111	0.008	2.153	0.167
	0.004	2.034	0.140	0.01	2.266	0.176
	0.006	2.101	0.151	0.012	2.355	0.185
100	0.002	1.842	0.200	0.008	2.087	0.224
	0.004	1.897	0.209	0.01	2.192	0.238
	0.006	1.996	0.212	0.012	2.289	0.244

Viscometry. The viscosity measurements of inulin solutions were made in a calibrated two-limbed Ubbelohde viscometer placed in a thermostatted water bath with an average flow time of 190.4 s for 13 mL of water. The temperature in the bath was maintained within an uncertainty of ± 0.1 K. The measured densities were uncertain within ± 0.05 kg·L^{-1}. The solution flow time in the viscometer was taken after thermal equilibrium at each temperature. Each measurement was duplicated, and the mean value was recorded and used. The minimum flow time of the measurements was 191 s with an uncertainty of ± 0.1 s. The maximum uncertainty in viscosity was, therefore, ± 0.3 %.

Solubility. The turbidimetric experiments (i.e., point of solubility) were visually performed in an illuminated condition in a thermostatted water bath. In the actual experiment, IP was progressively added with a Hamilton microsyringe into 2 mL of aqueous inulin solution of varied concentrations, and their turbidity points were noted by comparing with the pure inulin solution against a bright background. The measurements were taken three times, and the mean values were used. The maximum uncertainty in the solubility measurements was estimated to be ± 6 % at the 95 % confidence limit.

Results and Discussion

Viscosity of Inulin in Water + DMSO and Water + IP Media. In our previous report,[17] [η] (intrinsic viscosity, i.e., the fractional change in viscosity of the polymer solution per unit concentration at infinite dilution) values of inulin in water and DMSO have been presented. Since inulin has been found to form globular aggregates in water and rod-like assembles in DMSO, with an appreciable difference in the [η] values, we have herein studied the viscosity behaviors of the biopolymer in mixed water + DMSO and water + IP media. The collected data on viscosity are presented in Tables 1 and 2.

$$\eta_{sp}/C = [\eta]_H + k[\eta]_H^2 C \tag{1}$$

where η_{sp} is the specific viscosity of the polymer solution ($\eta_{sp} = \eta_r - 1$ when η_r is the relative viscosity of the polymer), $[\eta]_H$ is the intrinsic viscosity by Huggins equation, k_H is the Huggins constant, and C is the inulin concentration in kg·L^{-1}.

Table 2. Viscosity (η) and Reduced Viscosity (η_{sp}/C) of Inulin Solution in the Water (1) + IP (2) Medium at 303 K

100 x_2	C / kg·L^{-1}	η / mPa·s	η_{sp}/C / L·kg^{-1}
1.6	0.001	1.029	0.052
	0.003	1.0398	0.051
	0.005	1.050	0.050
	0.007	1.060	0.049
	0.009	1.072	0.0478
3.2	0.001	1.262	0.062
	0.003	1.265	0.031
	0.005	1.249	−0.007
	0.007	1.233	−0.024
	0.009	1.199	−0.048

Figure 1 depicts the plots in terms of Huggins equation, and $[\eta]_H$ and k_H are presented in Table 3. The estimated $[\eta]_H$ and k_H were on the average uncertain within (± 5 and ± 11) %, respectively. The increasing DMSO content increased $[\eta]_H$, that is, the globular geometry of the polymer aggregates changed to the elongated type ultimately to form rod-like supra aggregated species in the pure DMSO medium.[17]

A check on the $[\eta]_H$ values of inulin was made by processing the viscosity results in terms of Kraemer's eq 2 in the following form.[18,19]

$$\ln \eta_r = [\eta]_K C \tag{2}$$

where $[\eta]_K$ is the intrinsic viscosity by Kramer's equation.

The Kraemer's plots at different DMSO content in the DMSO + water medium are presented in Figure 2. The $[\eta]_K$ values obtained by this procedure are also presented in Table 3. The $[\eta]_K$ was uncertain within ± 5 %. This form of Kraemer's equation has been also found to obey by different gums in salt solution.[20] The $[\eta]_H$ and $[\eta]_K$ fairly agreed with each other. The mean values ($[\eta]_M$) have been considered as the intrinsic viscosities of inulin in water and water + DMSO media. The $[\eta]_M$ was found to exponentially increase with DMSO content in the media. Equations 1 and 2 mean that $Lt_{C=0}\eta_{sp}/C = [\eta]_H$ and $Lt_{C=0}\eta_r/C = [\eta]_K$. Both of the equations are empirically formulated; a correlation between them is not expected. The

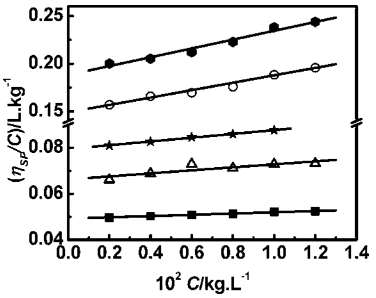

Figure 1. Huggins plot of $[\eta]_{sp}/C$ vs C at 303 K. ●, DMSO; ○, 6:1 (DMSO/water); ★, 1:1 (DMSO/water); △, 1:2 (DMSO/water); ■, water. Solvent compositions are in mole ratio.

Table 3. Dependence of [η] and k_H on Water (1) + DMSO (2) at 303 K

100 x_2	$[\eta]_H$ ($[\eta]_K$) / L·kg^{-1}	$[\eta]_M$ / L·kg^{-1}	k_H
0	4.92 (5.10)	5.0	1.13
25.0	5.86 (6.8)	6.33	2.12
33.3	6.63 (7.11)	6.87	1.50
50.0	7.96 (8.17)	8.08	1.27
66.7	11.0 (11.6)	11.3	1.09
85.7	14.9 (18.1)	16.5	1.75
100	18.8 (21.4)	20.1	1.30

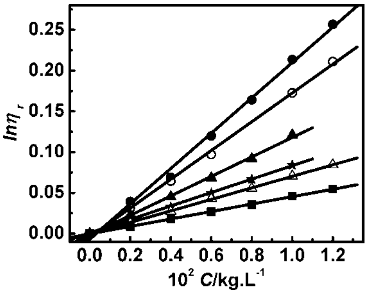

Figure 2. Kraemer's plot of ln η_r vs C at 303 K. ●, DMSO; ○, 6:1 (DMSO/water); ▲, 2:1 (DMSO/water); ★, 1:1 (DMSO/water); △, 1:2 (DMSO/water); ■, water. Solvent compositions are in mole ratio.

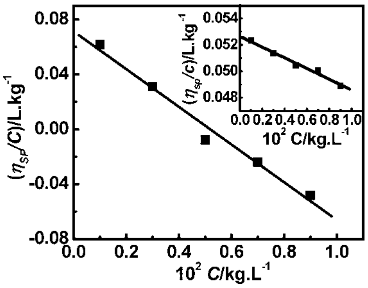

Figure 3. Huggins plot of $[\eta]_{sp}/C$ vs C at $x_{IP} = 0.032$ for inulin at 303 K. Inset: same plot at $x_{IP} = 0.016$.

near equivalence between $[\eta]_H$ and $[\eta]_K$ observed in practice for neutral polymers is also empirical in nature.

The presence of IP in water significantly affected the solubility of inulin. The solubility decreased with increasing IP concentration. At $x_{IP} = 0.03$, the solubility decrease was large. In this study, we used two solvent compositions, $x_{IP} = 0.016$ and 0.032, for viscosity study. The $[\eta]_H$ determination plots (exemplified in Figure 3) showed clear distinctions from water + DMSO. The plots produced negative slopes. The intercept yielded $[\eta]_H$ values of (5.25 and 7.13) L·kg^{-1} at $x_{IP} = 0.016$ and 0.032, respectively. Like water + DMSO, changes of geometry from globular to nonglobular form occurred also in the presence of IP. The negative slope and hence the negative k_H values were unusual observations. It somewhat paralleled the results on lysozyme in the water + DMSO medium,[21] where also with increasing [DMSO], $[\eta]_H$ increased with fairly large negative k_H values. Globular and compact lysozyme became denatured (elongated) by the action of DMSO to result in increased $[\eta]_H$, but how and why k_H values were negative was not explained in the report. A probable conceptual attempt has been herein made to account for the observation. Normally, relative viscosity increases with increasing solute concentration. In the Huggins procedure, the reduced viscosity $(\eta_r - 1)/C$ or $[\eta]_{sp}/C$ is plotted against concentration. Essentially, the plot represents a change in specific viscosity per unit concentration against the solution concentration of the polymeric species. The system which would show a lower increment in viscosity than expected with the increase in concentration should produce a declining viscosity per unit concentration with a negative slope in the Huggins plot. The effect of the solute on the structure of the solvent medium as well as its desolvation can increase the solution fluidity to make an onward decline in the reduced viscosity to make the k_H negative. This phenomenon probably occurred in the lysozyme study in the water + DMSO[21] medium as well as in the present study of inulin in the water + IP medium. Further elaborate viscosity or fluidity studies of inulin in the water + IP medium under varied environmental conditions are wanted for rationalization and quantification.

Table 4. Solubility of Inulin (*S*) in the Water (1) + IP (2) Medium at Different Temperatures

T/K	100 x_2	S/kg·L^{-1}	100 x_2	S/kg·L^{-1}
303	12.0	0.0064	5.04	0.0408
	8.61	0.0224	3.36	0.0522
	6.50	0.0309	2.25	0.0612
308	11.98	0.0062	4.50	0.0471
	9.68	0.0138	3.69	0.0516
	5.66	0.0380	2.07	0.0602
313	10.6	0.0056	3.85	0.0431
	8.36	0.0126	2.92	0.0532
	5.72	0.0318	1.51	0.0654
318	9.10	0.0060	4.82	0.0329
	7.06	0.0151	3.74	0.0429
	6.19	0.0234	1.28	0.0643
323	8.56	0.0051	3.47	0.0434
	7.67	0.0111	2.63	0.0538
	4.45	0.0334	1.16	0.0667

Solubility of Inulin in Water + IP Medium. Inulin has moderate solubility in water (≈ 0.10) at 303 K. The solubility decreased with the increasing presence of IP in water. At $x_{IP} = 0.032$, the solubility became ≈ 0.01. We have studied the energetics of the solution of the polysaccharide inulin by measuring its solubility at different concentrations of IP in water at five different temperatures, (303, 308, 313, 318, and 323) K. The collected data of solubility measurements are presented in Table 4. The solubility showed a fairly linear decrease with the inverse of temperature (Figure 4). Processing the data in the light of van't Hoff eq 3 helped to calculate the standard enthalpy of solution (ΔH_S^0). Thus,

$$\mathrm{d}\ln x_{In}/\mathrm{d}(1/T) = \Delta H_S^0/R \tag{3}$$

where x_{In} is the solubility of inulin expressed in mole fraction unit, R is the gas constant, and T is the absolute temperature.

The dependence of ln x_{In} on T^{-1} was found to be fairly linear, yielding ΔH_S^0 from the slope (plots are not shown to save space). The values were found to be (2.06, −2.65, −12.1, −39.1, and −84.9) kJ·mol^{-1} for $x_{IP} = 0$, 0.025, 0.05, 0.075, and 0.1, respectively. ΔH_S^0 in water was weakly endothermic and became more and more exothermic by the increasing presence of IP in solution. The solubility of inulin in the water + IP medium produced associated or aggregated species that produced the release of heat to make the process exothermic.

Conclusion

Inulin has a fairly aqueous solubility; it is also liberally soluble in DMSO but very poorly soluble in IP. The molecular aggregation of inulin depends on the solvent medium which determines its $[\eta]$ value. $[\eta]$ is at a minimum in water, increases

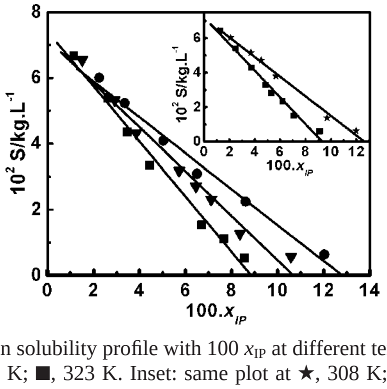

Figure 4. Inulin solubility profile with 100 x_{IP} at different temperatures. ●, 303 K; ▼, 313 K; ■, 323 K. Inset: same plot at ★, 308 K; ■, 318 K.

in water + DMSO, and is at a maximum in DMSO. [η] is fairly high in the water + IP medium. The solubility of inulin decreases with temperature (a hydrophobic effect), and the process is weakly endothermic. In the water + IP medium, the process becomes fairly exothermic.

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