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Calculation of viscometric constants, hydrodynamic volume, polymer–solvent interaction parameter, and expansion factor for three polysaccharides with different chain conformations

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Abstract—The viscometric constants, K and a, for three polysaccharides: hydroxyethylcellulose (HEC); hydroxypropylcellulose (HPC); and chitosan, were calculated at 30 °C using intrinsic viscosity, $[\eta]$ and molecular weight (M_n, M_w, M_z) data. The polydispersity correction factor, q_{MHS}, and hydrodynamic volume for each polymer sample were also calculated. The value of q_{MHS} for the polymer samples was taken into account in the calculation of the viscometric constants. The polymer–solvent interaction parameters for the three polysaccharides were estimated by both semiempirical and numerical methods using intrinsic viscosity and molecular weight data. Hydrodynamic expansion factors were also estimated using the latter data. The quality of the solvents for the three polymers was compared using exponent a, polymer–solvent interaction parameter, and expansion factor data.

This study resulted in the following constants for:

(1) HEC with weight-average-molecular weight range, M_w (36–511 kDa) in 0.05 mol L^{-1} $NaNO_3$ ($a = 0.600$; $K = 3.516 \times 10^{-3}$).
(2) HPC with M_w range (12–56 kDa) in (0.05 mol L^{-1} Na_2SO_4; pH 7.0) ($a = 1.080$; $K = 1.404 \times 10^{-5}$).
(3) chitosan with M_w range (141–327 kDa) in 0.83 mol L^{-1} CH_3COOH/0.3 mol L^{-1} NaCl ($a = 0.885$; $K = 1.464 \times 10^{-4}$).

The values of 0.60, 1.08, and 0.885 for exponents a indicate that HEC, HPC, and chitosan behave as a flexible random coil, linear and extended conformations, respectively. The values of exponents a for the three polysaccharides appear to be inversely related to their K values. The results of the expansion factor were consistent with the results of exponent a and polymer–solvent interaction parameters.

Keywords: Hydroxyethylcellulose; Hydroxypropylcellulose; Chitosan; Viscometric constants; Polymer–solvent interaction parameter; Expansion factor

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1. Introduction

Polysaccharides are generally classified based on their natural occurrence, chemical structure; solubility; or physicochemical properties. Cellulose and its derivatives consist of β-D-glucopyranosyl units with β-D-(1→4) linkages. Hydroxyethylcellulose (HEC) is a neutral and water soluble cellulose ether.[1,2] HEC and hydroxypropylcellulose (HPC) are hygroscopic, and the amount of water absorption by each cellulose derivative depends on its degree of substitution (DS).[3] HPC is more hydrophobic than HEC due to the presence of the methyl group on the side chain. HPC is soluble in water and organic solvents depending on its DS. In concentrated solutions, HPC exhibits lyotropic liquid crystalline behavior.[4] HEC finds application mainly based on its water solubility. It is used as a thickener and emulsifier in adhesives, cosmetics, paper, and textile industries.[5,6] HEC and its derivatives are also used in textile, paint, mineral, cements, and pharmaceutical industries. HPC

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is used as wetting, thickening, and binding agents, and it is used for formulation of hair sprays, cosmetics, pharmaceuticals, and personal-care items.[7] Chitosan is a copolymer of 2-amino-2-deoxy-D-glucose (glucosamine) and 2-acetamido-2-deoxy-D-glucose (*N*-acetyl glucosamine). The cationic nature of chitosan in acidic medium is unique among polysaccharides. It is safe, non-toxic, and biodegradable.[8] It exhibits diverse biological activities, as well as film- and fiber-forming properties. It has potential for applications in many areas such as food, agriculture, medicine, and cosmetics.[9,10]

Various properties of polymers are closely related to their molecular weights and molecular weight distribution (MWD). Average-molecular weights (M_n, M_v, M_w, and M_z) of polymers are determined by various methods (High Performance Liquid Chromatography/Size Exclusion Chromatography, HPLC/SEC equipped with different detectors such as light scattering, differential refractometer and differential viscometer; osmometry; viscometry; and sedimentation). Among various methods, viscometry is a simple method and requires an easy-to-use apparatus. The estimation of the molecular weight of polymers during polymer processing at a short time is critical in manufacturing. Determination of M_v is based on an Mark-Houwink-Sakurada (MHS) relationship. The determination of M_v requires measurement of the intrinsic viscosity of the polymer, $[\eta]$, in a solvent with the known Mark–Houwink–Sakurada (MHS) equation constants, a and K.

The constants are used (1) to determine the viscosity-average molecular weight, M_v; (2) to construct an SEC universal calibration curve; (3) to determine the hydrodynamic volume of polymers, $[\eta]$ M_v; (4) to interpret the data in SEC; and (5) to transform MWD and M_w data from standard polymers to unknown polymer samples that are structurally different from standard polymers.

The second virial coefficient, A_2, is an important parameter for a polymer–solvent system. Generally, A_2 is determined from osmometry or light-scattering techniques. The intrinsic viscosity can be used to estimate the polymer–solvent interaction parameter. The interaction parameter obtained from the intrinsic viscosity data is proportional to the A_2 value. Few attempts have been made to estimate the polymer–solvent interaction parameter from intrinsic viscosity data. In this study, the intrinsic viscosity data were used to determine a polymer–solvent interaction parameter and expansion factor.

The objectives of this work were (1) to determine the values of K and a, for the three polysaccharides (broad MWD of HEC and chitosan, and HPC having relatively narrow MWD), taking into account the polydispersity of the polymers; (2) to determine M_v and the hydrodynamic volume for each polymer sample; (3) to determine the polymer–solvent interaction parameter by two (semiempirical and numerical) methods and the expansion factor for each polymer.

2. Theoretical considerations

2.1. Calculation of viscometric constants and polydispersity correction factor, q_{MHS}

The value of $[\eta]$ varies with M_v for a homologous series according to the Mark–Houwink–Sakurada (MHS) equation[11,12]

$$[\eta] = K \cdot M_v^a \tag{1}$$

The symbols that appear in Eq. 1 and other equations are defined in Table 1. Determination of constants, K and a, from the intrinsic viscosity data requires a series of monodisperse polymer samples with the known molecular weight or a series of polydisperse polymer samples with the known viscosity-average molecular weights, M_v. In general, M_v is not experimentally accessible, whereas other average molecular weights are determined by different experimental methods. Eq. 1 can be rearranged and results in a modified MHS equation as follows:[16,17]

$$[\eta] = KM_v^a = K(M_v/M_w)^a \cdot M_w^a = Kq_{\mathrm{MHS}}M_w^a \tag{2}$$

The value of q_{MHS} is a statistical function of molecular weight distribution. The value of q_{MHS} varies from one sample to another because it is a function of a and average-molecular weights (M_v, M_w). The value of q_{MHS} is determined from (M_v/M_w).^{a} Alternatively, the value of q_{MHS} can be calculated using a numerical method and other average molecular weights (M_n, M_w, M_z) according to[13–15]

$$q_{\mathrm{MHS}} = (M_w/M_n)^b(M_z/M_w)^c \tag{3}$$

On the whole, the correction factor, q_{MHS}, is a function of exponent a, and average-molecular weights (M_n, M_v, M_w, M_z) (see Eqs. 2 and 3). The precision of the q_{MHS} value depends on the precision of both exponent a and average-molecular weights.

2.2. Calculation of the polymer–solvent interaction parameter

The second virial coefficient, A_2, is a measure of the solvent strength for a particular polymer. It can be considered as a polymer–solvent interaction. A number of equations that describe the relationship between polymer and solvent have been proposed. The equations contain a parameter that expresses the interaction between polymer and solvent. A semiempirical relation between second virial coefficient, A_2, and intrinsic viscosity has been already proposed as follows:[16,17]

$$[\eta] = [\eta]_\theta + 0.50 \cdot A_2M^{0.5} \tag{4}$$

Stockmayer and Fixman[16] proposed the following equation:

Table 1. Definition of symbols and abbreviations

Symbol	Definition	Equations
M_v	Viscosity-average molecular weight	1
K	Intercept for MHS equation. It is constant for a given solute–solvent–temperature system at a definite molecular weight range	1
a	Exponent for MHS equation. It is constant for a given solute–solvent–temperature system at a definite molecular weight range	1
M_w	Weight-average molecular weight	2
MHS	Mark–Houwink–Sakurada	1
q_{MHS}	Polydispersity correction factor	2, 3
M_n	Number-average molecular weight	3
M_z	z-Average (diffusion average) molecular weight	3
b	Constant, it is an empirical polynomial function of MHS exponent a	3
c	Constant, it is an empirical polynomial function of MHS exponent a	3
A_2	Second virial coefficient	4, 7
θ solvent	Ideal solvent for a polymer	4–6, 9–10
$[\eta]_\theta$	Intrinsic viscosity in θ-solvent	4, 9–10
K_θ	Unperturbed parameter	5, 6
B	Proportional to polymer–solvent interaction parameter	5, 6
N_0	Avogadro's constant	7
$[\eta]$	Intrinsic viscosity in a solvent	1–7, 9–10
ψ	Constant, proportion to excluded volume and expansion factor and called interpenetration function	7, 8
ϕ	Universal viscosity constant or Flory–Fox viscosity constant	7
α	Flory's expansion factor or viscosity expansion factor	9, 11, 12
z	Excluded volume parameter	11, 12
$\bar{z}$	z/α^3	12

$$[\eta] = K_\theta \cdot M^{0.5} + 0.51 \cdot B \cdot M \tag{5}$$

The equation can be rearranged as follows:

$$\frac{[\eta]}{M^{1/2}} = K_\theta + 0.51 \cdot B \cdot M^{1/2} \tag{6}$$

Alternatively, the following equation[18,19] has been proposed for the calculation of A_2 using intrinsic viscosity data.

$$A_2 = \frac{4\pi^{3/2} \cdot N_0[\eta]\psi}{6^{3/2} \cdot \phi_0 \cdot M_v} \tag{7}$$

In which ψ is called the interpenetration parameter and it is a function of $\bar{z}$. The following numerical method has been used to estimate the value for ψ:[20]

$$\psi = 0.547[1 - (1 + 3.903.\bar{z})^{-0.4683}] \tag{8}$$

This numerical procedure for the calculation of ψ is based on intermolecular and intramolecular theories of interaction.[21] To calculate the value of ψ, one should determine a value for α using Eq. 9[22,23]

$$\alpha^3 = [\eta]/[\eta]_\theta \tag{9}$$

where $[\eta]_\theta$ is determined from Eq. 10:[22]

$$[\eta]_\theta = K_\theta \cdot M^{0.5} \tag{10}$$

The value of z is calculated by the substitution of the value of α into Eq. 11:[24]

$$\alpha^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \tag{11}$$

The value of $\bar{z}$ is then obtained according to Eq. 12:[19]

$$\bar{z} = z/\alpha^3 \tag{12}$$

The value of $\bar{z}$ is then substituted in Eq. 8 to estimate a value for ψ. The value of A_2 is calculated by substitution of ψ and other parameters in Eq. 7.

2.3. Calculation of the hydrodynamic volume and expansion factor

In an ideal solvent, the intrinsic viscosity of a polymer is determined from Eq. 10. The dimensions and volume of the polymer in a good solvent expand by a factor of α and α,[3] respectively. This is because the intramolecular interactions between polymer segments decrease with an increase in quality of solvents.[22,23] The following equation is obtained by combination of Eqs. 9 and 10.

$$[\eta] = K_\theta \cdot M^{1/2} \cdot \alpha^3 \tag{13}$$

3. Materials and methods

3.1. Materials

HEC with a broad MWD ($36 \leqslant M_w \leqslant 511$ kDa; $2.19 \leqslant M_w/M_n \leqslant 5.22$), HPC having relatively narrow MWD ($12 \leqslant M_w \leqslant 56$ kDa; $1.61 \leqslant M_w/M_n \leqslant 1.93$), and chitosan with a broad MWD ($141 \leqslant M_w \leqslant 327$ kDa; $1.91 \leqslant M_w/M_n \leqslant 5.54$) and the degree of N-acetylation

(DA), of 22.5 ± 2.5% (American Polymer Standards Corporation, Mentor, OH, USA) were used in this study. The MWD of the HPC samples is narrower than that of HEC and chitosan samples.

3.2. Determination of intrinsic viscosity and average-molecular weights

The intrinsic viscosities of the polymers solutions were measured at 30 °C in 0.05 mol L^{-1} $NaNO_3$ for HEC; 0.05 mol L^{-1} Na_2SO_4 at pH 7.0 for HPC; and 0.83 mol L^{-1} CH_3CO_2H/0.30 mol L^{-1} NaCl for chitosan. The average molecular weights (M_n, M_w, M_z) and intrinsic viscosities of the polymer samples (HEC; HPC; and chitosan) have been determined by the American Polymer Standards Corporation. These values are listed in Table 2. SEC was used to determine different average molecular weights (M_n, M_w, and M_z) values. A differential refractometer and a differential viscometer were used as detectors. Since SEC separates polymers by hydrodynamic volume, and an online differential viscometer provides the value of intrinsic viscosity over entire molecular weight distribution, it thus became possible to calibrate the SEC systems with known standards and get several average molecular weights (M_n, M_w, M_z) of unknown polymers by construction of a universal calibration curve ($[\eta]$ M vs elution volume).

3.3. Calculation of viscometric constants and the polydispersity correction factor, q_{MHS}

The values of viscometric constants, a and K, and the polydispersity correction factor, q_{MHS}, were calculated using a modified MHS equation through a numerical method. The calculation of the constants using the numerical method involves several consecutive steps (calculation of b and c; calculation of q_{MHS}; and calculation of MHS constants, a and K). The procedure for the calculation viscometric constants is illustrated in Chart 1.

3.4. Calculation of the polymer–solvent interaction parameter and expansion factor

The polymer–solvent interaction parameters, B, for the three polysaccharides were determined by using Eq. 6 via the construction of ($[\eta]/M_v^{1/2}$) versus $M_v^{1/2}$. Alternatively, the value of A_2 was calculated by using Eq. 7 and the numerical method described in Section 2.2. The value of α for each polysaccharide was determined using the intercept of the latter plot and Eqs. 9 and 10. The procedures for the calculation of interaction parameter, B, and expansion factor by a semiempirical method and second virical coefficient by a numerical method are shown in Charts 2 and 3, respectively.

Table 2. M_n, M_w, M_z, and $[\eta]$ data for hydroxyethylcellulose, chitosan, and hydroxypropylcellulose samples given by American Polymer Standard Corporation

Sample	Hydroxyethylcellulose				Chitosan				Hydroxypropylcellulose		
	M_n (kDa)	M_w (kDa)	M_z (kDa)	$[\eta]^{(1)}$ (dL g^{-1})	M_n (kDa)	M_w (kDa)	M_z (kDa)	$[\eta]^{(2)}$ (dL g^{-1})	M_n (kDa)	M_w (kDa)	$[\eta]^{(3)}$ (dL g^{-1})
1	168.5	510.6	942.0	8.463	99.40	326.7	486.2	9.765	28.8	55.7	1.895
2	205.0	449.0	705.0	7.812	27.00	218.1	506.4	6.703	21.9	37.5	1.285
3	157.3	425.0	720.6	7.411	47.40	217.6	375.0	9.473	18.8	32.4	1.095
4	147.4	380.0	633.8	6.834	28.40	160.8	378.8	5.613	17.9	29.5	0.975
5	23.30	121.7	370.1	3.686	33.70	141.4	300.6	4.508	12.7	20.5	0.630
6	11.40	36.00	90.15	1.500					10.4	17.0	0.530
7									7.20	12.0	0.370

(1) $[\eta]$ in 0.05 mol L^{-1} $NaNO_3$ at 30 °C; (2) $[\eta]$ in 0.83 mol L^{-1} CH_3CO_2H/0.3 mol L^{-1} NaCl at 30 °C; and (3) $[\eta]$ in 0.05 mol L^{-1} Na_2SO_4 (pH 7) at 30 °C.

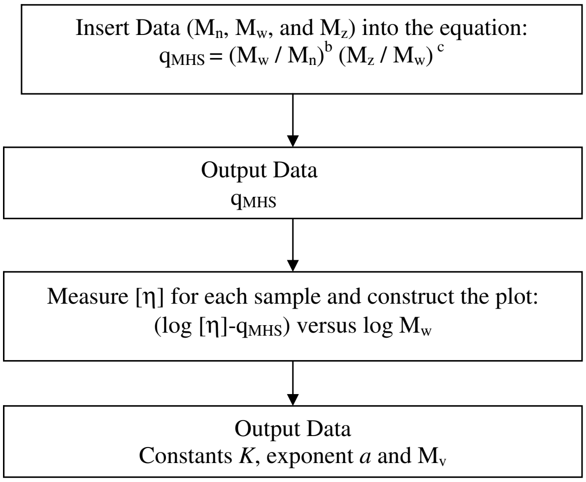

Chart 1. Procedure for the calculation of viscometric constants (K and a) and viscosity-average molecular weight (M_v).

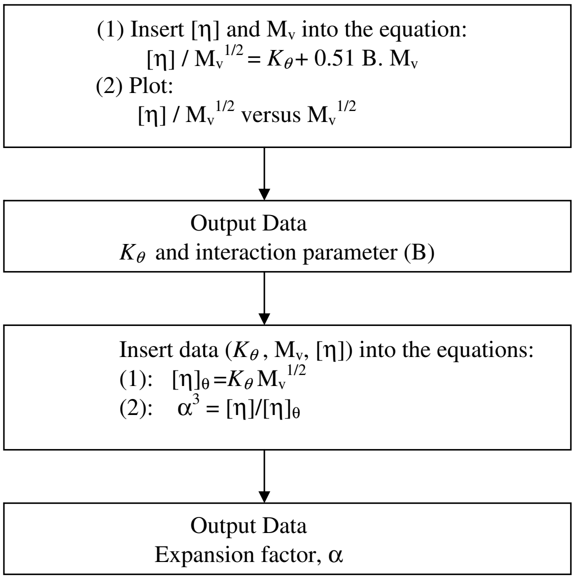

Chart 2. Procedure for calculation of expansion factor (α) and interaction parameter (B).

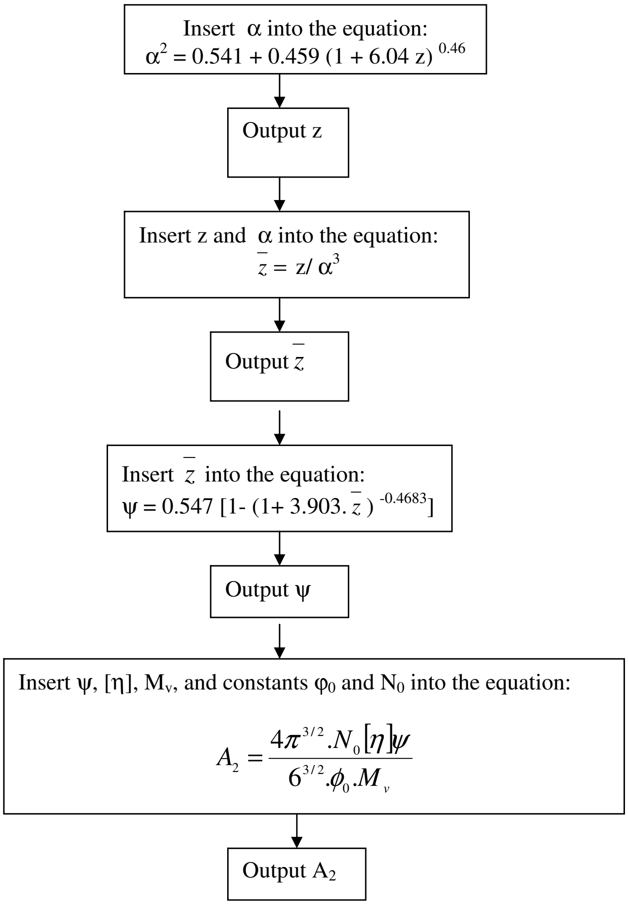

Chart 3. Calculation of second virial coefficient, A_2, by numberical method using intrinsic viscosity data.

4. Results and discussion

4.1. Viscometric constants

Figure 1 shows (log[η]–log$q_{\rm MHS}$) versus log$M_{\rm w}$ for HEC. The values of 0.600 and 2.86×10^{-3} were obtained for a and K, respectively. The value of $q_{\rm MHS}$ for each polymer sample was calculated and is given in Table 3. The values of $q_{\rm MHS}$ varied from 0.80 to 0.93. The resulting MHS equation for HEC in 0.05 mol. L^{-1} NaNO$_3$ at 30 °C with $M_{\rm w}$ range of 36–511 kDa is as follows:

$$\begin{aligned}[\eta] &= 3.516 \times 10^{-3} M_{\rm v}^{0.600} \\ &= 3.516 \times 10^{-3} q_{\rm MHS} \cdot M_{\rm w}^{0.600} \qquad (14)\end{aligned}$$

where [η] is expressed in dL g^{-1}.

The values of z-average molecular weights, $M_{\rm z}$, are not available for the series of HPC. The value of $q_{\rm MHS}$ for this series was calculated by assuming the following equation:

$$M_{\rm z}/M_{\rm w} = M_{\rm w}/M_{\rm n} \qquad (15)$$

This equation is valid for a symmetrical (Gaussian) curve, which is obtained from size-exclusion chromatography. Such a curve is usually obtained for a narrow or Gaussian distribution.[15,25] Calculation of the constants by taking into account the polydispersity of polymer samples results in higher precision for the constants compared to ignoring the polydispersity. Figure 2A shows (log[η]–log$q_{\rm MHS}$) versus log$M_{\rm w}$ for HPC. The values of $q_{\rm MHS}$ and $M_{\rm v}$ for HPC samples were calculated and presented in Table 3. Eq. 16 is proposed for HPC with $M_{\rm w}$ in the range of 12–55.7 kDa and an average value of 1.031 for $q_{\rm MHS}$ in (0.05 mol L^{-1} Na$_2$SO$_4$; pH 7.0) at 30 °C:

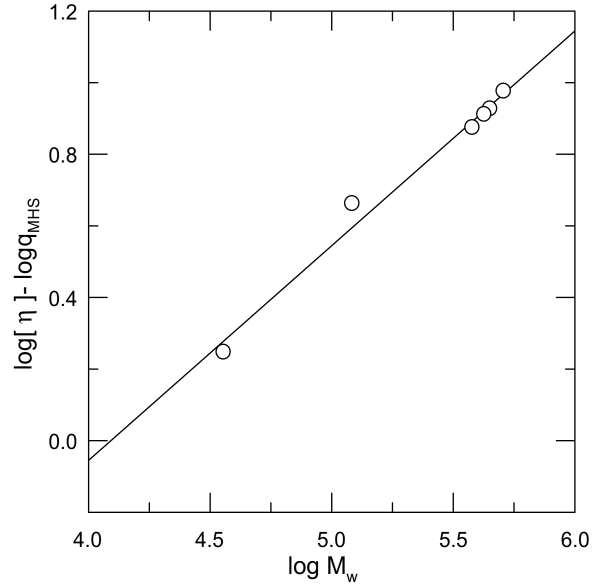

Figure 1. $(\log[\eta]–\log q_{\mathrm{MHS}})$ as a function of $\log M_{\mathrm{w}}$ for a broad MWD series of hydroxyethylcellulose samples in $0.05\,\mathrm{mol\,L^{-1}}$ $\mathrm{NaNO_3}$ at 30 °C and M_{w} range of 36–511 kDa.

$$[\eta] = 1.404 \times 10^{-5} M_{\mathrm{v}}^{1.080} = 1.339 \times 10^{-5} \cdot M_{\mathrm{w}}^{1.080} \quad (16)$$

The plot of $\log[\eta]$ versus $\log M_{\mathrm{w}}$ (by ignoring polydispersity) for the above-mentioned series of HPC resulted in values of 1.085 and 1.375×10^{-5} for the slope and intercept (Fig. 2B), respectively. The nearly identical values for the slopes and intercepts were obtained for the two plots (Figs. 2A and B). This is due to the near-unity of the exponent a. When the values of M_{v} and M_{w} are identical, the value of exponent a equals unity or vice versa.

Figure 3 shows $(\log[\eta]–\log q_{\mathrm{MHS}})$ versus $\log M_{\mathrm{w}}$ for a broad MWD series of chitosan in $0.83\,\mathrm{mol\,L^{-1}CH_3COOH}/0.3\,\mathrm{mol\,L^{-1}}$ NaCl at 30 °C. The values of 0.885 and 1.464×10^{-4} were obtained for a and K, respectively. The experimental points did not properly fit on the curve, and the regression value for the plot was found to be ($R^2 = 0.79$). The average value of q_{MHS} was found to be 0.954.

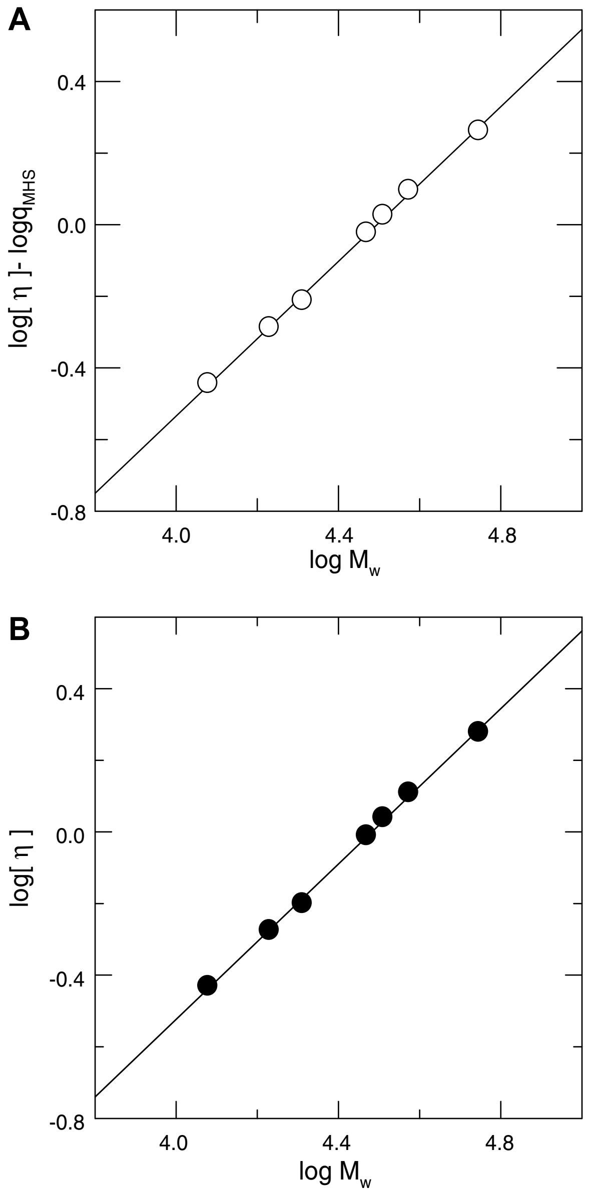

Figure 2. $(\log[\eta]–\log q_{\mathrm{MHS}})$ as a function of $\log M_{\mathrm{w}}$ for relatively a narrow MWD series of hydroxypropylcellulose in ($0.05\,\mathrm{mol\,L^{-1}}$ $\mathrm{Na_2SO_4}$; pH 7.0) at 30 °C with M_{w} range of 12–56 kDa.

$$[\eta] = 1.464 \times 10^{-4} M_{\mathrm{v}}^{0.885} = 1.397 \times 10^{-4} \cdot M_{\mathrm{w}}^{0.885} \quad (17)$$

Table 3. The values of q_{MHS}, M_{v}, and $[\eta]\ M_{\mathrm{v}}$ for hydroxyethylcellulose, chitosan, and hydroxypropylcellulose samples

Sample	Hydroxyethylcellulose			Chitosan			Hydroxypropylcellulose		
	M_{v} (kDa)	$[\eta]\ M_{\mathrm{v}} \times 10^{-3}$ dL mol^{-1}	q_{MHS}	M_{v} (kDa)	$[\eta]\ M_{\mathrm{v}} \times 10^{-3}$ dL mol^{-1}	q_{MHS}	M_{v} (kDa)	$[\eta]\ M_{\mathrm{v}} \times 10^{-3}$ dL mol^{-1}	q_{MHS}
1	614.4	5199.7	0.896	284.7	2780.1	0.971	56.45	106.98	1.037
2	537.7	4200.5	0.926	186.0	1246.8	0.936	39.39	50.616	1.030
3	492.4	3649.2	0.911	275.1	2606.0	0.960	33.97	36.562	1.031
4	430.2	2940.0	0.914	152.2	854.30	0.949	30.50	29.738	1.028
5	153.7	566.54	0.804	118.8	535.55	0.946	20.36	12.827	1.027
6	34.32	51.480	0.850				17.35	9.1955	1.028
							12.44	4.6028	1.029

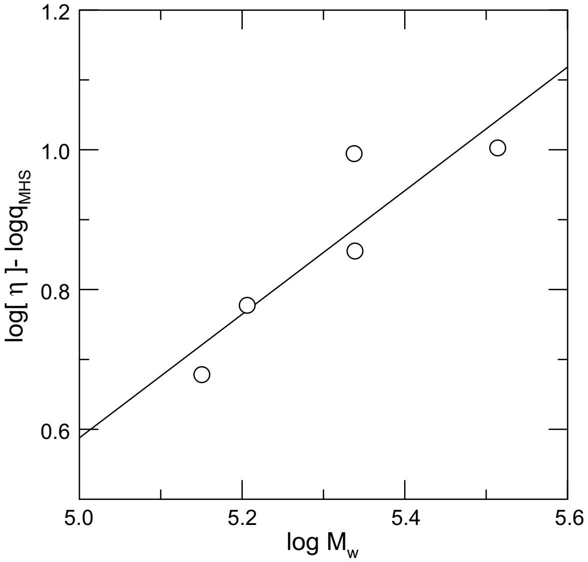

Figure 3. (A) $\log[\eta]$–$\log q_{\mathrm{MHS}}$) as a function of $\log M_{\mathrm{w}}$; and (B) $\log[\eta]$ as a function of $\log M_{\mathrm{v}}$, for a broad MWD series of chitosan samples in 0.83 mol L^{-1} CH_3CO_2H/0.3 mol L^{-1} NaCl at 30 °C with M_{w} range of 141–327 kDa.

Alternatively, the values of the constants for chitosan in the solvent were estimated using the two recently proposed equations[26] as follows:

$$\text{Exponent } a = [0.6202 + 0.699x/(0.4806 + x)] + [0.003(T - 20)] \quad (18)$$

$$\log K \cdot 10^{+5} = -5.7676 \cdot \text{Exponent } a + 5.9232 \quad (19)$$

where x equals [DA/pH·μ], with DA, the degree of acetylation of chitosan; pH of the chitosan solution; μ, ionic strength of the solvent; and T, the temperature of the polymer solution (in Celsius, °C). The value of x for chitosan (DA 0.225) in the solution (pH 2.42; $\mu = 0.34$) was calculated ($x = 0.2735$). The values of constants using the two equations above were found to be ($a = 0.904$, $K = 5.12 \times 10^{-5}$). The values of 0.885 and 1.464×10^{-4} are more reliable than those estimated from the two Eqs. 18 and 19. This is because several factors affecting the correct values for the constants have not been taken into consideration by the authors who reported several MHS equation constants for chitosans. A detailed explanation on the calculation of the correct values for the constants has been published elsewhere.[26] The advantages of the proposed procedure over the classical or numerical procedure are that it does not need to determine $[\eta]$ and the average molecular weights (M_{n}, M_{w}, M_{z}, M_{v}). The two proposed equations can be used for the estimation of the constants with a reasonable deviation when the solvent–temperature system is known.

Low amounts of salts in aqueous solutions were used to measure the intrinsic viscosities of HEC and HPC. While the concentration of salt for measurement of intrinsic viscosity of chitosan was high. The hydroxyl groups in cellulose contribute to strong intra- and intermolecular hydrogen bonds and prevent its solubility in water and other polar solvents. When cellulose is converted into cellulose ethers, the ether substituent groups (ethyl or propyl) disrupt the hydrogen bonds and increase its solubility and its hydration. At certain degrees of substitution, the insoluble cellulose is converted into a water-soluble colloid.[3]

A small value of the exponent ($a = 0.60$) was obtained for HEC, whereas the value for HPC was relatively high ($a = 1.08$). A less extended conformation ($a = 0.885$) than that of HPC was obtained for chitosan. All the three polysaccharides possess a β-(1→4)-glycosidic linkage. In a good solvent, the polysaccharide chains with β-(1→4)-glucosidic linkages behave like a linear chain. The nature of the solvent and its interaction with the polymer would have an impact on the polymer conformation. Flory's theory on θ-solvent does not take into consideration any specific interactions between solvent and polymer. If no major difference exists in polymer–solvent interactions, the conformation is flexible and the polymer behaves like synthetic polymers. In the presence of polar–polar interactions, the intrinsic viscosity of a polymer solution is greater, and the polymer conformation is larger than that of flexible polymers. Generally, the intrinsic viscosity and conformation of polysaccharides are different from synthetic polymers due to the presence of several polymer–solvent interactions.

The exponent a for HEC (DS 0.88) in water and cadoxen (an alkali solvent) at 25 °C was reported to be 0.87 and 0.79, respectively.[13,27] In contrast to the literature values, the value of exponent a found in the present study is low ($a = 0.60$). Salts such as sodium nitrate or sodium sulfate have a great affinity for water. The addition of salts to aqueous polymer solutions such as cellulose derivatives reduces the hydration of hydrophilic polymers, and thus the polymers are partially hydrated due to the great affinity of salts for hydration and consequently favor for polymer–polymer interactions.[3,28] This results in a low value for exponent a. The low coil extension in an aqueous salt solution may arise from the ionic-type forces possible between salt and the hydroxyl groups of the monomer units. Salt may locate between polymer chains and play the role of a bridge between polymer chains and promote aggregation. It may also arise from side chain hydrophobic interactions between ethyl groups of macromolecule chains. On the whole, the interactions between polymer chains in aqueous salt solution are stronger than in water. Therefore, one can conclude that water at 25 °C is a better solvent than an aqueous salt solution for HEC.

The interactions of polymer–solvent or polymer–polymer vary widely for the different cellulose derivatives depending on both the nature of the polymers and the nature of added salts to the solvent at a certain solution temperature.[3] Both the amounts of water required for hydration of the cation and anion of the salt (as a component of the solvent) and the amount of water required for hydration of hydrophilic moieties of the polymer (having both hydrophilic and hydrophobic moieties) should be taken into consideration to evaluate polymer–polymer and polymer–solvent interactions.[3,28]

In this study, the value of exponent a is found to be 1.08 for HPC, which is in agreement with the literature value ($a = 1.17$).[13] These values indicate that the polymer in both solvents behave as a stiff conformation. The intrinsic viscosity presented in this manuscript was measured in 0.05 mol L^{-1} Na_2SO_4 with pH 7.0 at 30 °C, whereas the corresponding data reported in the literature were carried out in ethanol at 25 °C. As HPC contains both hydroxyl and $–OCH_2CH(OH)CH_3$ groups, it has a combination of hydrophobic and hydrophilic characters. Since HPC is an amphiphilic polymer, the solubility of HPC decreases with an increase in temperature. This is attributed to a gradual loss of polymer–solvent interaction, and thus is less favorable for the interaction between the polymer and the solvent. The HPC–water system exhibits phase separation at elevated temperatures. The temperature at which phase separation occurs is referred to as the cloud point. HPC is water soluble up to 38 °C and becomes insoluble above 45 °C. Studies show that an aqueous HPC solution exhibits a typical lower critical solution temperature (LCST) behavior, generally upon heating above 40 °C.[3,29,30] Thermodynamically, low temperature is favored for polymer–solvent interactions, which leads to a negative enthalpy of polymer–solvent mixing. Phase separation occurs with increasing temperature due to the more unfavorable entropy contribution to the free energy. If one considers only temperature as a variable, the solvent at 25 °C is a better solvent, and the quality of the solvent decreases (the exponent a decrease from 1.17 to 1.08) as temperature increases. However, a combination of several variables (added salt to the solvent, temperature, DS, polymer concentration, molecular weight of polymer) influencing hydrophilic, hydrophobic, and hydrogen interactions should be taken into consideration to determine the quality of the solvent. HPC has a tendency to be highly crystalline in bulk form and forms a stiff conformation in a good solvent.[4,31] In ethanol as a solvent for HPC, two types of interactions are present: (1) a hydrophobic interaction between the ethyl group of the solvent and the propyl group of the polymer; and (2) a hydrophilic interaction between the hydroxyl group of ethanol and the hydroxyl groups of HPC. These interactions would yield a stiff conformation for HPC ($a = 1.17$). In an aqueous salt solution as a solvent for HPC, the level of hydrophilic interaction between hydroxyl groups of the monomer units and hydroxyl groups of water is varied by the addition of salt in pure water at a constant DS, polymer concentration and molecular weight of HPC.

Chitosan possesses both hydroxyl and amine groups. Amine groups of chitosan can take up a proton in an acidic medium[32] at pHs <6.5. The solution properties of chitosan as a polyelectrolyte depend strongly on the degree of dissociation of the ionizable groups (NH_3^+ in acidic medium) and differ significantly from those of neutral polymers. The conformation of chitosan changes with pH, temperature or added salts.[26,33] In salt-free aqueous solution, chitosan exhibits a more extended conformation and produces higher solution viscosities than those of nonionic polymers because of electrostatic repulsions among the positive charges distributed along the backbone of the macromolecules. The addition of salt to the solution results in a smaller conformation due to screening effects. At high amounts of salt, the viscosity of chitosan solutions will approach that of nonionic polymers.[34–36] The values of MHS equation constants, a and K, for chitosan in various solvent systems published in the literature have been determined by many authors over the past 30 years. These values were compared, reviewed, and published recently.[26] Among various solvent systems reported in the literature, three following solvent systems [(1) 0.33 mol L^{-1}. HAc/0.3 mol L^{-1} NaCl; (2) 0.1 mol L^{-1} HAc/0.2 mol L^{-1} NaCl; and (3) 0.25 mol L^{-1}HAc/0.25 mol L^{-1}NaAc], were selected to compare with the solvent used in this study [0.83 mol L^{-1} HAc/0.3 mol L^{-1} NaCl]. The exponents a and DA for the three polymer–solvent systems have been reported to be (1) 1.02 (DA% = 20–22); (2) 0.93 (DA% = 20); and (3) 0.79 (DA% = 21–26), respectively. The value of exponent a obtained in this study was 0.88 (DA% = 22.5). The conformation and hydrodynamic volume of chitosan in dilute solutions are strongly dependent on the DA and ionic strength.[33,37] It has already been shown that the exponent a increased with increasing in the DA.[26] The values of the DA for chitosans in the three polymer–solvent systems (1, 2, and 3) are approximately the same as the DA for chitosan used in this study. The major differences in the three polymer–solvent systems, which are largely affected by the value of exponent a, are the amount of salts. The amount of salts used in the three solvent systems varied from 0.2 to 0.3 mol L^{-1}, whereas the amount of salt in the solvent used in this study was 0.3 mol L^{-1}. As it was explained above, the addition of salt to the polymer solution has a screening effect on electrostatic repulsions and results in a smaller chain conformation at higher salt concentration. If one takes into consideration all the parameters affecting the value of exponent a (amount of salt, pH and DA), it is preferable to use the semiempirical Eq. 18 for the determination of exponent a. The value of 0.88 that was obtained in this study is in agreement with the value estimated from the semiempirical Eq. 18 ($a = 0.90$), and it is also in agreement with the literature data.

4.2. Hydrodynamic volume and expansion factor

The value of M_v for each polymer sample of the three polysaccharides was calculated and is given in Table 3. The values of M_v and M_w for each HPC sample are closer to each other compared to chitosan and HPC samples. This is because the exponent a for HPC is close to unity (see Tables 1 and 2). The values of q_{MHS} for the HPC series are closer to 1.0 compared to HEC and the chitosan series, and the values of q_{MHS} for the HEC series are smaller than those of the chitosan series. These data indicate that the HPC series is the narrowest among the three polysaccharides, and the HEC series is the widest. However, the HPC series in comparison to synthetic polymers having narrow polydispersity is still wide.

The viscosity expansion factors for each HEC and chitosan series were calculated and are presented in Table 4. The expansion factors for the chitosan series are larger than those of the HEC series. A large value of expansion factor α was attributed to the high value of the exponent a. The value of α characterizes the goodness of a solvent. The greater value of α indicates a stronger level of polymer–solvent interactions and a large value for hydrodynamic volume.

The viscosity expansion factors for HEC (MS 1.67, DS 0.88) were reported to be in the range ($\alpha = 1.34$–1.75) in water and ($\alpha = 1.21$–1.48) in cadoxen with a slight increase with increasing of molecular weight of the polymer.[27,38] In the present study, the expansion factor for HEC was found to be in the range ($\alpha = 1.01$–1.04) with a slight increase for an increasing molecular weight of the polymer. Thus, the expansion factor in an aqueous salt solution was the smallest, and it was the greatest in water. The expansion factor for chitosan in [0.83 mol L^{-1}HAc/0.3 mol L^{-1} NaCl] was found to be in the range ($\alpha = 1.15$–1.20) (see Table 4).

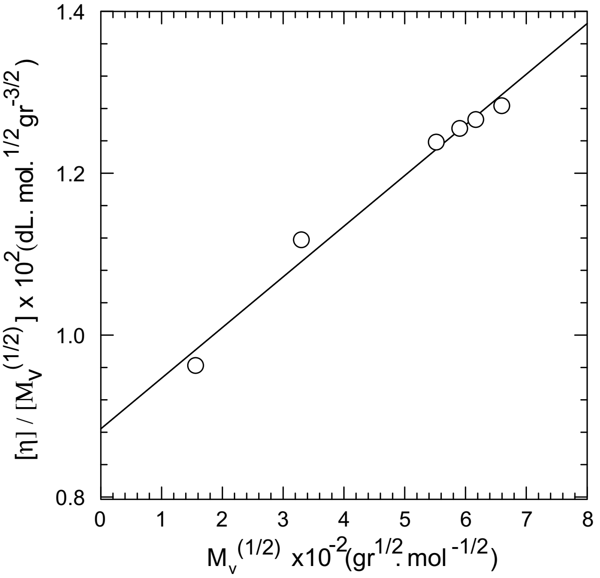

Figure 4. The value of $([\eta]/M_v^{1/2})$ versus $M_v^{1/2}$ for hydroxyethylcellulose.

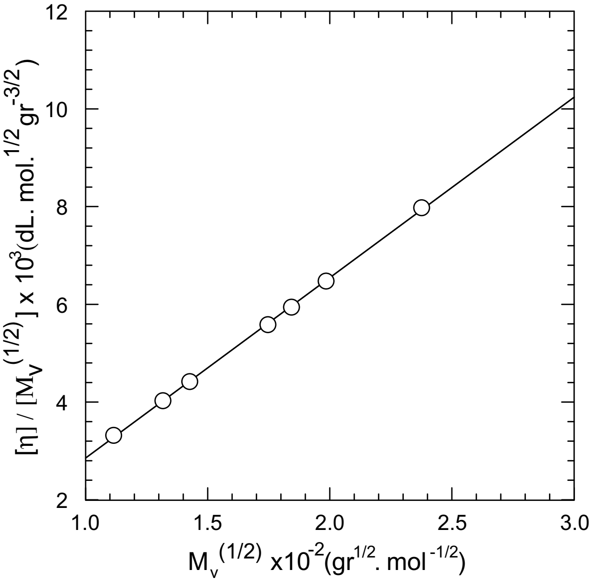

Figure 5. The value of $([\eta]/M_v^{1/2})$ versus $M_v^{1/2}$ for hydroxypropylcellulose.

Table 4. The values of M_v, $[\eta]$, $[\eta]_\theta$, expansion factor, α and second virial coefficient, A_2 (calculated from the numerical method) for each hydroxyethylcellulose and chitosan sample

	Hydroxyethylcelluloses						Chitosan					
Sample	M_v (kDa)	$[\eta]$ (dL g^{-1})	$[\eta]_\theta$ (dL g^{-1})	α^3	α	$A_2 \times 10^4$ mol dL g^{-2}	M_v (kDa)	$[\eta]$ (dL g^{-1})	$[\eta]_\theta$ (dL g^{-1})	α^3	α	$A_2 \times 10^4$ mol dL g^{-2}
1	614.4	8.463	5.8313	1.1322	1.042	2.46	284.7	9.765	1.9303	1.7166	1.197	7.5
2	537.7	7.812	5.4549	1.1272	1.041	2.55	186.0	6.703	1.5605	1.6256	1.176	15
3	492.4	7.411	5.2204	1.1239	1.040	2.58	275.1	9.473	1.8975	1.7091	1.196	19
4	430.2	6.834	4.8793	1.1188	1.038	2.61	152.2	5.613	1.4115	1.5843	1.166	23
5	153.7	3.686	2.9163	1.0812	1.026	2.82	118.8	4.508	1.2470	1.5348	1.154	45
6	34.32	1.500	1.3781	1.0286	1.009	0.19						

4.3. Polymer–solvent interaction parameter

The plot of $([\eta]/M_v^{1/2})$ versus $M_v^{1/2}$ for the three polysaccharides are shown in Figures 4–6. The values for inter-

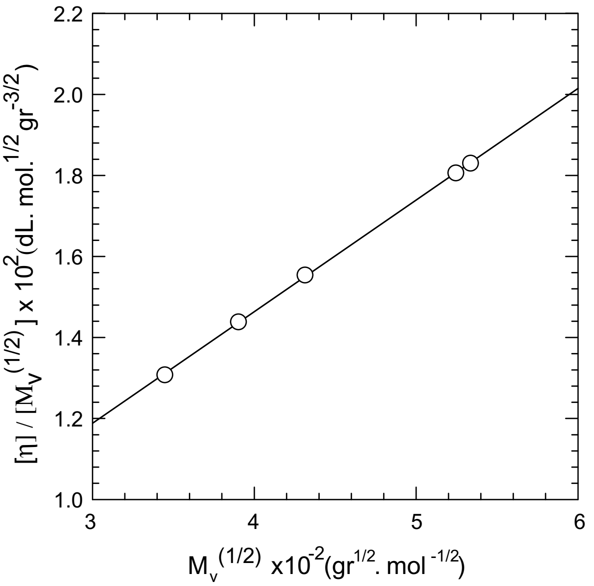

Figure 6. The value of $([\eta]/M_v^{1/2})$ versus $M_v^{1/2}$ for chitosan.

action parameters, *B* (slopes/0.51), intercepts (K_θ) and regression coefficients (R^2) of the linear plots are given in Table 5. The value of *B* is the highest for HPC and is the lowest for HEC. These results indicate that the polymer–solvent interaction for HPC is the strongest and is the weakest for HEC. The high values for regression coefficients for the three Figures 4–6 indicate the existence of a strong correlation between $([\eta]/M_v^{1/2})$ and $M_v^{1/2}$.

A negative value of K_θ for HPC was obtained. Theoretically, the value of K_θ is positive. According to the concept of the theta (θ) condition, the unperturbed dimensions of a nonpolar polymer in a solvent do not depend on the nature of the solvent, but in the cases of polar polymer–polar solvent systems, the unperturbed dimensions vary considerably with the nature of the solvent and the polymer. The change in unperturbed dimensions can be attributed to the change in flexibility of a macromolecular chain as well as to polymer–solvent interactions. Thus similar unperturbed dimensions may not be expected for a polymer in different solvent–temperature systems. The extrapolation to unperturbed conditions for HPC in 0.5 mol L^{-1} NaCl solution yielded in a straight line. However, the extrapolation in 0.1 mol L^{-1} has shown a curvature. This could be due to the fact that the amount of salt is not enough to eliminate the non-size-exclusion mechanism in the region of low molecular weights.[29] These authors have not reported values for K_θ. The Stockmayer–Fixman equation (Eq. 5) is valid for flexible polymers. The unperturbed dimensions of a flexible polymer in any solvent can be estimated from Eq. 5 or 6, assuming that the draining effects are negligible.[39] An extrapolation of $[\eta]/M^{1/2}$ against $M^{1/2}$ leads to erroneous values of unperturbed dimensions if the MHS exponent *a* exceeds 0.8. This is due to partial draining, chain stiffness, or both.[40–42] Extrapolations of viscosity data in good solvents even for flexible chains should be used with great caution.[40] Deviation from the experimental values has been attributed in part to the fact that the semiempirical equation is only valid over a limited range of *a* values.[41] A plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ may give a good straight line, and linear extrapolation to $M = 0$ yields a negative intercept, that is, Eq. 5 or 6 is not applicable for extended, linear, or stiff conformation. In such cases, $[\eta]/M_v^{1/2}$ increases more rapidly than $M_v^{1/2}$ and reliable data for unperturbed dimensions (θ-conditions) can not be acheived using intrinsic viscosity data and Eqs. 5 and 6. In such cases, other methods such as light scattering can be employed to determine unperturbed dimensions. To achieve reliable data for unperturbed dimensions (θ-conditions) under the above-indicated conditions, one should determine additional data such as the radii of gyration to augment the viscosity data. A negative value for intercept of the plot $[\eta]/M^{1/2}$ against $M^{1/2}$ was obtained for chitosan (DA% = 21) in 0.33 mol L^{-1}HAc/0.3 mol L^{-1} NaCl at 21 °C.[43] The exponent *a* of the MHS equation for chitosan in the above-mentioned solvent system has been reported to be 1.02, suggesting that the polymer in solution has a stiff conformation. Tanaka[40] observed curvature in the plot ($[\eta]/M^{1/2}$ versus $M^{1/2}$ for some flexible polymers in good solvent systems. This author noted that the curvature causes errors in the extrapolation to $M = 0$, even if nonlinear extrapolation is used, and unperturbed dimensions obtained in this way are often unreliable.[40]

The values of A_2 for the HEC and chitosan series were calculated by a numerical method and are presented in Table 4. The value of A_2 was not calculated for the HPC series because of the negative value of K_θ. The values of A_2 for the chitosan series were found to be larger than that of HEC series. The values of B calculated by the semiempirical method ($[\eta]/M_v^{1/2}$ vs $M_v^{1/2}$) was in agreement with the result of A_2 determined by the numerical method.

The second virial coefficients for HEC in water at 25 and 38 °C have been already reported[27] to be 4.3×10^{-4} and 2.9×10^{-4} mol dL g^{-2}, respectively. These authors have also shown that the A_2 for HEC

Table 5. Interaction parameters, *B*, Flory's constants, K_θ, and regression coefficients, R^2, determined from Figures 4–6 for three polysaccharides

Polymer	Interaction parameter B × 10^5 (dL g^{-1})	$K_\theta \times 10^3$	R^2
HEC	1.23	8.84	0.980
HPC	7.24	−8.38	0.999
Chitosan	5.41	3.62	0.999

in water slightly decreased with increasing molecular weight. The average value for A_2 obtained in the present study was 2.6×10^{-4} mol dL g^{-2}, and the value of A_2 as a function of molecular weight was identical within experimental error. The value of A_2 found in the present study is smaller than that of the literature values. This disparity is due to the differences in the quality of the solvent. It has been already explained that water is a better solvent compared to aqueous salt solution for HEC. The disparity could be also due to the difference in the methods of A_2 determination. Brown et al.[27] have used light scattering as an experimental method, whereas the author of this study has estimated the A_2 from the intrinsic viscosity data using a theoretical–experimental equation. The light-scattering method results in a more reliable value than the semi-experimental one.

5. Conclusions

This study resulted in the following MHS equations at 30 °C for a broad series of HEC in 0.05 mol $\mathrm{L^{-1}NaNO_3}$ with M_w range of 36–511 kDa; a series of HPC in (0.05 mol $\mathrm{L^{-1}Na_2SO_4}$; pH 7.0) with M_w range of 12–56 kDa and polydispersity smaller than 2; and a broad MWD series of chitosan in 0.83 mol $\mathrm{L^{-1}}$ $\mathrm{CH_3CO_2H}$/0.3 mol $\mathrm{L^{-1}}$ NaCl, with M_w range of 141–327 kDa.

$[\eta] = 3.516 \times 10^{-3} M_v^{0.600} = 3.516 \times 10^{-3} q_{\mathrm{MHS}}\ M_w^{0.600}$ (a broad series of hydroxyethylcellulose)

$[\eta] = 1.404 \times 10^{-5} M_v^{1.080} = 1.404 \times 10^{-5} q_{\mathrm{MHS}}\ M_w^{1.080} = 1.339 \times 10^{-5} M_w^{1.080}$ (relatively a narrow series of hydroxypropylcellulose)

$[\eta] = 1.464 \times 10^{-4} M_v^{0.885} = 1.397 \times 10^{-4} \cdot M_w^{0.885}$ (a broad series of chitosan)

where q_{MHS} is the polydispersity correction factor and $[\eta]$ is the intrinsic viscosity in dL g $^{-1}$.

The polymer–solvent interaction parameter, B, is determined for the three polysaccharides. The value of B was the highest for HPC and the lowest for HEC. A good correlation between ($[\eta]/M_v^{1/2}$) and $M_v^{1/2}$ was achieved for the three polysaccharides. The values of B calculated by the semiempirical method ($[\eta]/M_v^{1/2}$ vs $M_v^{1/2}$) were in agreement with the result of A_2 determined by the numerical method, that is, the values of A_2 and B for chitosan were larger than those of HEC series. The expansion factor for chitosan was also larger than that of HEC. The results of the expansion factor for the three polysaccharides were consistent with the results of the exponent a and the polymer–solvent interaction parameter.

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