CHAPTER-III

Thermodynamics/Hydrodynamics of Aqueous Polymer Solutions and Dynamic Mechanical Characterization of Solid Films of Chitosan, Sodium Alginate, Guar Gum, Hydroxyethyl cellulose and Hydroxypropyl Methylcellulose at Different Temperatures

ABSTRACT

In this chapter, experimental densities and viscosities of five important carbohydrate polymers viz., chitosan, sodium alginate, guar gum, Hydroxyethyl cellulose and hydroxypropyl methylcellulose have been measured in aqueous media at five different temperatures and at nine weight fractions. Using the density data, excess molar volumes have been computed. Mathematical equations are proposed to calculate the activity, which agreed well with the experimental data. Viscosity data at different concentrations of carbohydrate polymer solutions have been used to calculate the viscosity average molecular weight of the polymers. Thin free standing films of these polymers have been prepared by solution casting method and were tested for dynamic mechanical behavior as well as glass transition of the polymers were evaluated by dynamic mechanical thermal analyzer and thermogravimetry, respectively.

Results of this chapter have been accepted by “Carbohydrate Polymers” (2005).
III. 1. INTRODUCTION

Flory and Huggins have studied thermodynamic properties of polymer solutions extensively in the early forties [1,2]. In later years, innumerable studies [3-6] have been made to extend both theoretical and experimental aspects of these concepts to many polymer systems in order to understand the intermolecular interactions between the polymer and the solvent molecules. Such studies are useful to predict solution properties of polymers before their intended applications in various disciplines [7-10]. Other approaches to predict thermodynamic properties of polymer solutions include hard-sphere, non-compressible, compressible lattice, off-lattice models as well as models based on the generalized van der Waals partition function [11,12]. In the compressible model, free volume concept was used in understanding thermodynamics of phase behavior in polymers. In this aspect, several new theories have emerged in addition to equation of state theory of Prigogine and coworkers [13] as well as others [14,15] that led to a newer understanding of solution properties and phase behavior of long-chain polymers. Even though many more celebrated theories have been advanced in this direction over the past many decades, yet such studies have remained active, since these are quite fundamental in nature and are useful in understanding the theory of polymer solutions [15-18].

In order to understand polymer-solvent interactions, many sophisticated experimental techniques such as light scattering, ultracentrifuge, etc, have been employed [19,20]. However, conventional techniques like densitometry and viscometry have been quite useful to obtain thermodynamic information [21,22].
In the earlier literature, synthetic polymers have been the main target for such investigations due to their ease of preparation, applications in industries, etc. However, due to the recent environmental pollution concerns, naturally available carbohydrate polymers are considered in place of synthetic polymers for various applications. In particular, carbohydrate polymers like sodium alginate (NaAlg), chitosan (CS), hydroxy ethyl cellulose (HEC), hydroxypropyl methylcellulose (HPMC) and guar gum (GG) have been used in drug delivery applications due to their biocompatibility [23]. Also, they find applications as membranes in liquid or gaseous mixture separations [24-27]. In these applications, it is helpful to predict their thermodynamic properties in aqueous media since such a data-base would be useful in formulating drug delivery systems as well as to prepare separation membranes.

Carbohydrate polymers of this study are abundant in nature. Of these, NaAlg occurs as a white to yellowish brown filamentous, grainy, and granular or in powdered form, which is used as a stabilizer, thickener, gelling agent, and emulsifier in chemical/pharmaceutical industries. GG is a polysaccharide, a long chain biopolymer, made of sugar galactose and mannose. It is available as a white to yellowish odorless, available in different viscosity grades as well as in granule form. Depending upon its viscosity, it is used as a thickener and emulsifier in commercial food processing. It is also used in dressings, milk products and baking mixes. It finds usage in paper manufacturing, textiles, printing, cosmetics, and pharmaceuticals. Chitosan, a derivative of chitin, is manufactured commercially on a large scale from the outer shells of crustaceans. It is used in a wide variety of
forms including powder, solution or gel. HEC is water-soluble ether and is a non-ionic polymer that is compatible with a wide variety of other water-soluble polymers, which is used as a thickener in latex paints and paper finishes. HPMC is cellulose ether, derived from the alkali-treated cellulose by reacting with methyl chloride and propylene oxide. It is used as an emulsifier, thickening agent, stabilizer, and gellant and suspending agent.

The present investigation is an effort to understand the solution properties of these carbohydrate polymers by measuring their densities at different temperatures from 298.15 to 338.15K in order to evaluate excess molar volumes \((V^\text{E})\) and activity of 1% aqueous polymer solutions. Density results have been analyzed using the thermodynamic activity models derived from the Flory-Huggins theory [17], while excess molar volumes have been computed from density results. These results are discussed to understand thermodynamic interactions between the polymer-water systems. Mathematical equations are presented for data analysis to find an agreement between the activity of solvent computed by theory and experiments. The theory has the advantages that only density measurements are required to calculate excess molar volume and activity. Note that a similar study was made earlier by Eliassi et al., [28,29].

In the present chapter, carbohydrate polymers have been selected in view of their importance in biology and medicine. Viscosity data on all polymers have been obtained to understand hydrodynamic interactions and to compute molecular weights of the polymers. In addition, polymers were characterized in their thin film forms by dynamic mechanical thermal analyser (DMTA) and
thermogravimetry analyzer (TGA) to understand morphological characteristics and the transition behavior. Results of this study would be useful in seeking commercial applications of these polymers in medicine/separation science.

III. 2. THEORETICAL SECTION

Solution nonidealities of the mixtures can be represented by the activity coefficients that arise due to intermolecular interactions between components of the mixture. Thus, activity coefficient, $\gamma$, of a component can be derived from the thermodynamic equation,

$$RT \ln \gamma_i = 
\left( \frac{\partial g_E}{\partial n_i} \right)_{T,P,n_{i=1}}$$

(III.1)

where $g_E$ is molar Gibbs excess function and $n$ is total number of moles of the components given by:

$$n = \sum_{i=1}^{c} n_i$$

III. 2.1. Excess quantities

Molar Gibbs excess function is given by the relation,

$$g^E = u^E + P v^E - Ts^E$$

(III.2)

where $u^E$ is molar Gibbs excess internal energy, $v^E$ is molar excess volume, and $s^E$ is molar excess entropy. In order to obtain $\gamma_i$ at temperature, $T$ and pressure, $P$, the exact composition dependent functions for $u^E$, $v^E$, and $s^E$ are needed. Since attempts to obtain exact functionality for $g^E$ have not been successful and hence, the proposed activity models suffer from limitations imposed by the assumptions. In this regard, Margules and van Laar [14,15] equations, wherein it was tacitly

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assumed that $s^E = 0$, and no volume change was observed upon mixing i.e., $V^E = 0$. Thus, solution non-idealities were attributed to molecular interactions between pair molecules and functionality for $u^E$ was derived. In some cases, nonrandomness was considered to be the main cause of such deviations. Based on the original lattice model of Guggenheim, Flory [17] derived the expression for $s^E$ for polymer solutions. Flory considered the arrangement of polymer chains and solvent molecules in the lattice to derive an equation for $s^E$ in the following form:

$$\frac{s^E}{R} = -x_1 \ln \left[ 1 - \left( 1 - \phi_1 \right) \left( 1 - \frac{1}{r} \right) \right] - x_2 \ln \left[ r - \phi_2 \left( r - 1 \right) \right]$$

(III.3)

where $x_i$ and $\phi_i$ are mole fraction and volume fraction of solvent (1) and polymer (2), respectively; $r$ is number of segments of the polymer chain. The volume fraction, $\phi_i$, is expressed as,

$$\phi_1 = \frac{x_1 \nu_1}{x_1 \nu_1 + x_2 \nu_2} \quad \text{and} \quad \phi_1 = (1 - \phi_2)$$

(III.4)

The quantity, $r$ is defined as the ratio of molar volume of the polymer (2) to that of solvent (1) given by,

$$r = \frac{\nu_2}{\nu_1}$$

(III.5)

However, Flory [17], assumed that, $v^E = 0$ and hence, $g^E$ is expressed as:

$$g^E = u^E - s^E$$

(III.6)

where, $u^E$ was obtained from the Scatchard-Hildebrand equation [15]. In the present work, a simple model is used to predict solvent activities in polymer solutions.

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The excess molar volume was calculated from the experimental density values using,

\[ v^E = \frac{1}{\rho} - \left( \frac{w_1}{\rho_1} + \frac{w_2}{\rho_2} \right) \] (III.7)

where \( \rho \) is density of the polymer solution, \( w_1 \) and \( w_2 \) are weight fractions of components 1 and 2, respectively; \( \rho_1 \) and \( \rho_2 \) are respective of pure components densities. While using \( \rho \) values in Eq. (III.7), density results were fitted to polynomial equation of the type

\[ \rho \ (g/cm^3) = A + B\omega_2 + C\omega_2^2 + D\omega_2^3 \] (III.8)

where \( A, B, C, \) and \( D \) are coefficients \((g/cm^3)\) and \( \omega_2 \) is weight fraction of the polymer in solution. The values of coefficients were obtained by regression analysis using Marquardt equation [32] and these are given in Table III.2. By using Eqs, (III.7) and (III.8), \( v^E \) values were calculated and results are displayed in Figs. III.1 and III.2.

### III. 2.2. Activity model

Equation (III.1) can also be written in terms of mole fraction of the solvent \( (x_i) \) as:

\[ RT \ln \gamma_i = g_i + (1 - x_i) \frac{\partial g^E}{\partial x_i} \] (III.9)

Inserting Eq (III.2) into Eq (III.9), we get,
\[ RT \ln y_1 = u^E + P v^E - T s^E + (1 - x_i) \frac{\partial}{\partial x_i} (u^E + P v^E - T s^E) \]  

(III.10)

or

\[ RT \ln y_1 = [u^E + (1 - x_i) \frac{\partial}{\partial x_i} (u^E)] + [P v^E + (1 - x_i) \frac{\partial}{\partial x_i} (P v^E)] 
+ [-T s^E + (1 - x_i) \frac{\partial}{\partial x_i} (-T s^E)] \]  

(III.11)

From Eq (III.11), it can be seen that activity coefficient of the solvent \((y_1)\) can be divided as internal energy \((y_1^U)\), volume \((y_1^V)\), and entropy \((y_1^S)\) contributions:

\[ y_1 = y_1^U y_1^V y_1^S \]  

(III.12)

where each of the quantities are computed as,

\[ RT \ln y_1^U = u^E + (1 - x_i) \frac{\partial u^E}{\partial x_i} \]  

(III.13)

\[ RT \ln y_1^V = P v^E + (1 - x_i) \frac{\partial (P v^E)}{\partial x_i} \]  

(III.14)

\[ RT \ln y_1^S = -T s^E + (1 - x_i) \frac{\partial (-T s^E)}{\partial x_i} \]  

(III.15)

Activity of the solvent \((a_i)\) can be expressed as: \(a_i = x_i y_1\) and hence, we have

\[ x_i^3 y_1 = x_i^3 y_1^U x_i^3 y_1^V x_i^3 y_1^S \]  

(III.16)

so that \(a_i\) is given by,

\[ a_i = \frac{1}{x_i^2} (a_i^U a_i^V a_i^S) \]  

(III.17)

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where \( \alpha_1^U, \alpha_1^V, \) and \( \alpha_1^S \) are, respectively internal energy, volume, and entropy contributions to activity. By using Eq (III.14), excess volume part of activity of solvent can be calculated as

\[
\ln \alpha_1^V = \frac{P}{RT} (\nu^s + (1 - x_i) \frac{\partial \nu^s}{\partial x_i}) + \ln x_i
\]  

(III.18)

Excess enthalpy part of activity of solvent can then be derived from Eq. III. 3 to give,

\[
\ln \alpha_1^S = \ln \phi_i + (1 - \frac{1}{r})(1 - \phi_i)
\]  

(III.19)

However, internal energy part of activity is affected by molecular interactions that depend upon molecular rearrangements defined by entropy and molecular separations in terms of volume. Therefore, internal energy part of activity (\( \alpha_1^U \)) is a function of excess entropy as well as excess volume as seen in Eq. (III.17), which upon arrangement gives,

\[
\frac{\alpha_1^U}{x_i^2} = \frac{\alpha_1^U}{\alpha_1^V \alpha_1^S}
\]  

(III.20)

Right hand side of Eq. (III.20) can be expressed as:

\[
\frac{\alpha_1^U}{\alpha_1^V \alpha_1^S} = (\alpha_1^S \nu^s)(\alpha_1^V \nu^s)
\]  

(III.21)

where \( \nu^s_i \) and \( \nu^s_s \) are weighing factors. In the logarithmic form, Eq (III.20) can be written,
Similarly, Eq. (III.17) is expressed in logarithmic form,

$$\ln a_i = (1 + f_i^S) \ln a_i^S + (1 + f_i^V) \ln a_i^V$$  \hspace{1cm} (III.23)

By substituting for $a_i^V$ and $a_i^S$ from Eqs (III.18) and (III.19), respectively in to Eq. (III.23), we get

$$\ln a_i = f^C \left[ \ln \phi_i + (1 - \frac{1}{r})(1 - \phi_i) \right] + f^E \left[ \frac{P}{RT} \left( \nu^E + (1 - x_i) \frac{\partial \nu^E}{\partial x_i} \right) + \ln x_i \right]$$  \hspace{1cm} (III.24)

where $f^C = (1 + f_i^S)$ and $f^E = 1 + f_i^V$. Equation (III.24) can be expressed in terms of volume fraction ($\phi$) using Eq (III.4) to give the final equation for activity.

$$\ln a_i = f^C \left[ \ln \phi_i + (1 - \frac{1}{r})(1 - \phi_i) \right] + f^E \left[ \frac{P}{RT} \left( \nu^E + \phi_2 \left( \phi_1 + \frac{1}{r} \phi_2 \right) \frac{\partial \nu^E}{\partial \phi_1} \right) \right]$$
$$+ \ln \left( \frac{r \phi_1}{r \phi_1 + \phi_2} \right)$$  \hspace{1cm} (III.25)

In order to apply the above equation, we need density values of the polymer and solvent, their compositions in solution, and values of weighing factors, $f^C$ and $f^E$.

In the present research, we have used:

$$f^C = f^E = 0.5$$  \hspace{1cm} (III.26)

This gave the same weight to effects of entropy and volume contribution of activity to compute the activity of component, 1 in a given mixture.
III. 3 RESULTS AND DISCUSSION

III.3.1 Density, activity and excess molar volume

Density results of different polymers at different temperatures and concentrations (weight fractions) are presented in Table III.1. These data are fitted to Eq. (III.8) by the method of least squares to estimate the coefficients ($A$, $B$, $C$, and $D$) along with the correlation coefficient, $\sigma$ calculated as:

$$\sigma = \frac{100}{n} \sum_{i=1}^{n} \left[ \frac{\left( \rho_i^{\text{exp}} - \rho_i^{\text{cal}} \right)}{\rho_i^{\text{exp}}} \right]$$

(III.27)

where $n$ is number of experimental data; $\rho_i^{\text{exp}}$ and $\rho_i^{\text{cal}}$ are experimental and calculated densities using Eq. (III.8). These results are given in Table III.2. The calculated values of $V^e$ using Eq. (III.7) are presented in Table III.3. Activity data are compiled in Table III.4.
Table III. 1

Density (g/cm³) of different polymer solutions in water at different temperatures

<table>
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<tr>
<th>Wt fraction of polymer</th>
<th>298.15 K</th>
<th>308.15 K</th>
<th>318.15 K</th>
<th>328.15 K</th>
<th>338.15 K</th>
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Table III. 2

Estimated parameters of polynomial (Eq. III.8) for different polymers at different temperatures.

| Temperature (K) | Chitosan | | | Sodium alginate |
|-----------------|----------|----------|------------|-----------------|-----------------|
|                 | A        | B        | C          | D              | σ               |
| 298.15          | 1.1123   | 0.0027   | 0.0050     | 0.0004         | 0.0006          |
| 308.15          | 0.6950   | 0.2940   | 0.8393     | 0.0276         | 0.0392          |
| 318.15          | 0.8245   | -0.0605  | 0.9293     | 0.0306         | 0.0339          |
| 328.15          | 1.2329   | -1.0892  | 2.8260     | 0.0474         | 0.0393          |
| 338.15          | 0.6007   | 0.6291   | 2.0754     | 0.0589         | 0.0996          |
|                 |          |          |            |                |                 |

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Table III. 3

Excess molar volumes of different polymer solutions at different temperatures

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<th>338.15 K</th>
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**Hydroxy ethyl cellulose**

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**Guar gum**

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**Hydroxypropyl methylcellulose**

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CHAPTER III
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Table III. 4

Activity of different polymer solutions at different temperatures

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| Sodium alginate        |         |         |         |         |         |
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| 0.2                   | 1.0336  | 0.9995  | 0.9995  | 0.9993  | 0.9991  |
| 0.3                   | 1.0391  | 0.9984  | 0.9983  | 0.9982  | 0.9979  |
| 0.4                   | 1.0447  | 0.9959  | 0.9959  | 0.9958  | 0.9957  |
| 0.5                   | 1.0335  | 0.9899  | 0.9899  | 0.9899  | 0.9900  |
| 0.6                   | 1.0119  | 0.9743  | 0.9744  | 0.9746  | 0.9748  |
| 0.7                   | 0.9454  | 0.9275  | 0.9278  | 0.9285  | 0.9294  |
| 0.8                   | 0.7608  | 0.7795  | 0.7806  | 0.7822  | 0.7845  |
| 0.9                   | 0.3353  | 0.3918  | 0.3945  | 0.3958  | 0.3991  |

CHAPTER III
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**CHAPTER III**
The results of $V^E$ represent the deviations from ideal behavior. These are related to intermolecular interactions between water (solvent) and carbohydrate polymers. The $V^E$ values result from chemical, physical, and structural effects of polymers when they dissolved in aqueous media. Physical effects (dispersion forces) contribute to positive $V^E$; chemical and structural effects (specific interactions) contribute to negative $V^E$. In the present study, in all cases, the $V^E$ values exhibit positive deviations, indicating mild of dispersion-type interactions.

Figure III.1 displays the plots of $V^E$ vs. weight fraction ($w_1$) of the polymer for the five different polymers employed at five different temperatures. The $V^E$ values are found vary in the same range for CS, NaAlg and HEC at all the temperatures, whereas HPMC and GG have shown large positive $V^E$ values at 298.15K and 308.15K, which decreased considerably with further raise in temperature.

In these polymers (HPMC and GG), temperature has a considerable effect on $V^E$. For instance, when the temperature is raised from 318.15K to 338.15K, the $V^E$ values for GG become large as compared to HPMC. Nearly a four-fold increase in $V^E$ is observed at 328.15K and 338.15K as compared to $V^E$ from 298.15K and 318.15K. Such large positive $V^E$ values observed for GG is due to the breaking of hydrogen bonds of the associated polymer molecules in the presence of H-bonded water molecules.
Figure III. 2 displays the dependence of $V^E$ vs. $w_1$ for all polymers at different temperatures. It is noticed that considerable differences are observed for the dependence of $V^E$ on temperature depending upon the nature of the polymer. Notice that HPMC exhibits almost identical trends in $V^E$ between (298.15 and 338.15) K.

Figure III. 3 display the plots of activity $(a_1)$ vs. $w_1$ for all polymers at the studied temperatures. It is observed that temperature variations are distinct for activity calculations. Almost single curve is obtained within the studied temperature interval. In any case, the proposed model is reliable in predicting solvent activities of the binary polymer solutions as seen by the observed agreement.
Figure III.1. Excess molar volumes of different polymer solutions at different temperatures
Figure III. 2. Excess volumes of different polymers at different temperatures.
Figure III. 3. Activity coefficient of water in water and different polymers at different temperatures.
III. 3.2. Viscosity

Viscosities of polymer solutions determined at five different concentrations are compiled in Table III. 5, while the graphs of $\eta_{sp}/c$ and $\ln \eta_r/c$ vs concentration are displayed in Figure III. 4. The numerical data of intrinsic viscosity, $[\eta]$ and molecular weight, $M_n$ are given in Table III.6. Using the viscosity data and the well-known M.H.S relation [17]: $[\eta] = K M^a$, molecular weight of the polymers was calculated. The $K$ and $a$ values of the poly (vinyl pyrrolidone), (PVP) were taken as the standard to calculate molecular weights of all other carbohydrate polymers. Molecular weights of the polymers vary in the order: CS > HEC > HPMC > NaAlg > GG.

Table III.5
Viscosity data of polymer solutions

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<th>Concentration, $C$ (g/dL)</th>
<th>Flow time, $t$ (s)</th>
<th>$\nu t_0 = \eta_r$</th>
<th>$N = \eta_{sp}/c$</th>
<th>$L = \ln \eta_r/c$</th>
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</tr>
<tr>
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<td>Sodium alginate</td>
<td>[Flow time ((t_o)) for solvent water = 6.76 s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>20.83</td>
<td>3.08</td>
<td>41.6</td>
<td>22.5</td>
</tr>
<tr>
<td>0.10</td>
<td>41.73</td>
<td>6.17</td>
<td>51.7</td>
<td>18.2</td>
</tr>
<tr>
<td>0.15</td>
<td>62.56</td>
<td>9.25</td>
<td>55.0</td>
<td>14.8</td>
</tr>
<tr>
<td>0.20</td>
<td>83.39</td>
<td>12.34</td>
<td>56.7</td>
<td>12.6</td>
</tr>
<tr>
<td>0.25</td>
<td>104.22</td>
<td>15.41</td>
<td>57.6</td>
<td>10.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydroxy ethyl cellulose</th>
<th>[Flow time ((t_o)) for solvent water = 6.76 s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>8.06</td>
</tr>
<tr>
<td>0.10</td>
<td>9.72</td>
</tr>
<tr>
<td>0.15</td>
<td>11.37</td>
</tr>
<tr>
<td>0.20</td>
<td>13.02</td>
</tr>
<tr>
<td>0.25</td>
<td>15.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Guar gum</th>
<th>[Flow time ((t_o)) for solvent water = 6.76 s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>7.67</td>
</tr>
<tr>
<td>0.10</td>
<td>15.52</td>
</tr>
<tr>
<td>0.15</td>
<td>23.23</td>
</tr>
<tr>
<td>0.20</td>
<td>30.91</td>
</tr>
<tr>
<td>0.25</td>
<td>38.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydroxypropyl methylcellulose</th>
<th>[Flow time ((t_o)) for the solvent water = 6.76 s.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>8.95</td>
</tr>
<tr>
<td>0.10</td>
<td>18.21</td>
</tr>
<tr>
<td>0.15</td>
<td>27.16</td>
</tr>
<tr>
<td>0.20</td>
<td>36.15</td>
</tr>
<tr>
<td>0.25</td>
<td>46.21</td>
</tr>
</tbody>
</table>
Table III.6.

Results of viscosity and molecular weight of different polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Intrinsic viscosity $[\eta]$</th>
<th>Molecular weight $(\eta = K \cdot M^a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>15.96</td>
<td>2,63,883</td>
</tr>
<tr>
<td>NaAlg</td>
<td>39.5</td>
<td>1,22,594</td>
</tr>
<tr>
<td>HEC</td>
<td>3.65</td>
<td>2,16,400</td>
</tr>
<tr>
<td>GG</td>
<td>9.92</td>
<td>1,17,862</td>
</tr>
<tr>
<td>HPMC</td>
<td>13.13</td>
<td>1,89,555</td>
</tr>
</tbody>
</table>

[K and $a$ values of PVP are taken as standards for the calculation of molecular weight. $K = 39.3 \times 10^{-3}$ and $a = 0.59$]
Figure III. 4. Plots of $\eta_{BP}/c$ (•) and $\ln\eta_{BP}/c$ (○) versus concentration of different polymers in water (Chitosan in 2% acetic acid) at 30°C.
III. 3.3. Thermogravimetry analysis (TGA)

Thermal degradation profiles of CS, GG, HEC, HPMC, and NaAlg films are shown in Figure. III. 5. All polymers have shown single step degradation with an initial weight loss of about 1 to 7 % below 100°C due to release of moisture from the polymers. Of all the polymers studied, HPMC has shown higher thermal stability with the onset of degradation at 311°C, whereas NaAlg has shown the lowest thermal stability with an onset of degradation around 235°C. In general, thermal stability of the polymers followed the trend: HPMC > HEC > CS > GG > NaAlg. This trend is quite different than that observed for molecular weight dependence as discussed before. The % weight loss, onset and end-set degradation temperatures for various polymers are given in Table III.7.

III. 3.4. Dynamic mechanical thermal analysis (DMTA)

DMTA results of CS, NaAlg, GG, HEC, and HPMC have been studied in terms of loss tangent (tan δ) and storage modulus (E′) as a function of temperature (see Fig. 6). The tan δ and E′ values for various polymers are included in Table III.7. The polymer viz., NaAlg having the least thermal stability exhibited the highest value of tan δ (102.7 °C) and E′ (4.27 x 10⁹) compared to all other polymers. However, the weight loss of NaAlg was only 46.6 %, whereas HPMC exhibited highest thermal stability as well as highest % weight loss(69.5) compared to other polymers.
Table III.7
Results of $E'$, tan $\delta$, onset, end-set and % wt. loss of different carbohydrate polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E'$</th>
<th>tan $\delta$</th>
<th>Onset</th>
<th>End set</th>
<th>% wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEC</td>
<td>$4.09 \times 10^8$</td>
<td>45.1</td>
<td>289.72</td>
<td>392.98</td>
<td>60.2</td>
</tr>
<tr>
<td>NaAlg</td>
<td>$4.27 \times 10^9$</td>
<td>102.7</td>
<td>235.49</td>
<td>259.37</td>
<td>46.6</td>
</tr>
<tr>
<td>CS</td>
<td>$2.17 \times 10^9$</td>
<td>42.35</td>
<td>287.75</td>
<td>325.36</td>
<td>39.8</td>
</tr>
<tr>
<td>GG</td>
<td>$2.7 \times 10^9$</td>
<td>38.36</td>
<td>271.42</td>
<td>326.22</td>
<td>59.5</td>
</tr>
<tr>
<td>HPMC</td>
<td>$1.44 \times 10^9$</td>
<td>90.7</td>
<td>311.69</td>
<td>502.23</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Figure III.5. TGA thermograms of different carbohydrate polymers
Figure III. 6. $E'$ and $\tan \delta$ curves of different carbohydrate polymers
III. 4. CONCLUSIONS

The present study is a novel and unified approach to understand solution thermodynamics and hydrodynamics of five carbohydrate polymers in aqueous media. These polymers have a great relevance as controlled release matrices in drug delivery as well as membranes in separation science. Solution properties (density and viscosity) of the polymers studied are important in understanding their solution as well as film forming properties. The films of these polymers were subjected to DMTA and TGA analyses to understand their dynamic mechanical properties. The present study would have great relevance in application areas of the polymers, particularly in drug delivery and membrane science.
III. 5. REFERENCES


