

Intrinsic viscosities and Huggins constants of guar gum in alkali metal chloride solutions

Xiaodong Ma, Marek Pawlik *

Norman B. Keevil Institute of Mining Engineering, University of British Columbia, 517-6350 Stores Road, Vancouver, BC, Canada V6T 1Z4

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Abstract

The effect of lithium, sodium, potassium, and cesium chlorides on the properties of dilute guar gum solutions was investigated through viscosity measurements. The results showed that the intrinsic viscosity of guar gum is not significantly affected by the salts up to an electrolyte concentration of 4.1 mol/L. In the same ionic strength range, however, clear differences were observed between individual salts in their ability to influence the Huggins constant. At even higher electrolyte concentrations, only lithium and sodium chlorides markedly increased the intrinsic viscosity of the polymer, pointing towards the formation of a new type of structure in those solutions. The observed trends were attributed to the chaotropic (K^+ , Cs^+) or kosmotropic (Li^+ , Na^+) properties of the background salts. It was suggested that chaotropic electrolytes were capable of enhancing the dissolution of colloidal guar gum aggregates normally present in polysaccharide solutions under ambient conditions. On the other hand, the presence of high concentrations of kosmotropic ions led to enhanced aggregation of guar gum due to competitive hydration for free water molecules between the polysaccharide chains and the strongly hydrated cations. Comparative tests with the use of urea showed that the solute affects the behavior of dilute guar gum solutions in a way similar to NaCl, so its dispersing/hydrogen bond-breaking capabilities towards the polymer were not very clear in the studied system.

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1. Introduction

Guar gum is a natural non-ionic polysaccharide produced from the seeds of two annual leguminous plants, *Cyamopsis tetragonolobus* and *psoraloides*. The guar gum macromolecule is a chain of (1 → 4)-linked β -D-mannopyranose units with α -D-galactopyranose units connected to the mannose backbone through (1 → 6) glycosidic linkages. The poly-mannose chain is randomly substituted with galactose units at a mannose-to-galactose ratio of 1.8–1.0 (Painter, Gonzalez, & Hemmer, 1979; Whistler & Hymowitz, 1979). Because of the random nature of the substitution, the least substituted sections of the guar gum molecules show the greatest tendency to associate, while

the more densely substituted regions serve to solubilize the polymer chain (Dea, 1993). Guar gum does not form “truly molecular” solutions. Under normal conditions, aqueous solutions of guar gum contain a small fraction of undissolved colloidal aggregates and only a combination of high temperatures and pressures during the solution preparation stage results in a complete (or nearly complete) dissolution and hydration of the polymer (Picout, Ross-Murphy, Errington, & Harding, 2001). The size of such guar gum aggregates was found to be on the order of 10–100 μ m at guar concentrations as low as 0.038 wt% (Gittings et al., 2000, 2001). The heterogeneous nature of guar gum solutions makes their characterization quite difficult especially when the testing methods rely on light scattering.

Guar gum has a number of applications in the mining and mineral processing industry. In the froth flotation of base metal and platinum group metal ores, guar gum is used as a depressant of naturally hydrophobic waste miner-

* Corresponding author. Tel.: +1 (604) 827 5034; fax: +1 (604) 822 5599.
E-mail address: mpp@mining.ubc.ca (M. Pawlik).

als, such as talc. The role of the polysaccharide is to adsorb on the talc surface, render it hydrophilic, and prevent its flotation. A wide variety of modified guar gums are available for this application (Harris, Mapasa, Canham, & Bradshaw, 1999).

In another important flotation application, natural guar gum is employed as a “blinder” of water-insoluble, ultra-fine minerals in the froth flotation of potash ores. Canadian potash ores typically contain over 90% of the minerals sylvite (KCl) and halite (NaCl) with only a few percent of the so-called water-insoluble slimes, represented mostly by various clay and carbonate minerals. The objective of the process is to selectively separate sylvite from halite while completely rejecting the slimes. Since both sylvite and halite are highly soluble in water, the entire potash flotation process is carried out in a saturated KCl–NaCl brine. Sylvite is floated from halite with the use of a primary amine-based collector that also shows a high affinity towards the unwanted slimes. Therefore, the “blinding” action of guar gum in this high-ionic strength system relies on the adsorption of the polymer on the ultrafine minerals, thus forming a protective coating around these particles, and allowing the collector to selectively interact with the sylvite (KCl) crystals. In the absence of guar gum, the amine consumption would be very high and the selectivity of the amine-type collector towards KCl would drastically be reduced.

In relation to mineral processing applications, the adsorption of guar gum, and polysaccharides in general, on various minerals has been studied quite extensively (Liu, Zhang, & Laskowski, 2000; Shortridge, Harris, Bradshaw, & Koopal, 2000; Wang, Somasundaran, & Nagaraj, 2005). Ma and Pawlik (2005, 2006a) have recently shown that adsorption of the polysaccharide on quartz proceeds differently from KCl than from NaCl solutions, and the observed differences were attributed to the chaotropic and kosmotropic properties of K^+ and Na^+ cations, respectively. It should also be pointed out that very few studies have ever been published on guar gum adsorption from high ionic strength brines (Ma & Pawlik, 2006b; Pawlik & Laskowski, 2006) and the solution chemistry of the polymer in concentrated electrolytes is still poorly understood.

The main objective of this study is to gain insight into the behavior of guar gum in different electrolyte solutions of varying ionic strength through intrinsic viscosity measurements.

2. Experimental

2.1. Materials

A sample of guar gum, Rantec KP4000, was obtained from Rantec Corporation (Ranchester, WY, USA). The KP4000 is widely used by the Canadian potash industry as a slime blinder. First, a stock guar gum solution was prepared at a concentration of 1.8 g/L by mixing 0.9 g of raw

guar powder with 400 mL of distilled water at room temperature. The powder was slowly added into a vortex formed under thorough mixing with a magnetic stirrer. The guar–water suspension was then mixed for 4 h at room temperature. Finally, the volume was made up to 500 mL while mixing. In order to remove any insoluble residues, all stock guar gum solutions were centrifuged at 10,000g (Heraeus, Biofuge-primo centrifuge). Using the phenol–sulfuric acid method developed by Dubois, Gilles, Hamilton, Rebers, and Smith (1956) to measure the absorbance of guar gum solutions before and after centrifuging, it was found that the absorbance values did not decrease further after a centrifuging time of 30 min. Although the initial raw guar gum concentration (1.8 g/L) was arbitrarily chosen, it also greatly sped up and enhanced the efficiency of the centrifuging step due to the rather low viscosity of the centrifuged solution. The preparation method thus also showed that the KP4000 contained 12% of water-insoluble parts, a number that agrees very well with previously published data for a range of natural guar gums (Chatterji & Borchardt, 1981). Stock guar gum solutions were prepared daily to minimize biochemical degradation, and the actual guar concentration was calculated from the phenol–sulfuric acid assay.

The ionic strength of guar gum solutions was adjusted with lithium, sodium, potassium, and cesium chlorides, and with the salts obtained after evaporating a saturated potash brine. The brine was prepared from a potash ore (Lanigan mine, Saskatchewan) by dissolving the ore in warm distilled water. The resulting solution contained a large amount of suspended slimes which were allowed to settle over a period of 3 weeks. The clear brine was siphoned out and evaporated. A chemical analysis of the brine revealed the following concentrations of the main cations: Na^+ 4.4 mol/L, K^+ 1.7 mol/L, Ca^{2+} 0.040 mol/L, and Mg^{2+} 0.015 mol/L. The brine can thus be treated as a 6.1-M solution of KCl–NaCl.

Cesium chloride (crystalline, 99.9% pure) was supplied by Aldrich. Lithium, sodium, and potassium chlorides were ACS-certified chemicals from Fisher. Viscosity measurements were also made using urea (ACS) provided by Alfa Aesar.

2.2. Viscosity measurements

Dilute guar gum solutions were made by mixing a stock solution (after centrifuging) in distilled water with concentrated salt solutions, or by adding crystalline salts to a guar solution in distilled water and taking a concentration correction for a change in the solution volume (for saturated salt solutions).

The viscosities of guar gum solutions were measured using Cannon–Fenske capillary viscometers (Schott Geräte GmbH, Germany). After preparation, the solutions of desired polymer and salt concentration were left overnight (10–12 h). Then, 7-ml aliquots of the tested solutions were transferred to a capillary viscometer, the viscometer was

then placed in a water bath (set at 24 °C) for 30 min. Tests at higher temperatures (45, 70, and 90 °C) were performed only in distilled water. For high-temperature experiments, guar gum solutions were first tested at 24 °C, then the temperature of the bath was raised to the desired value without removing the capillary (still containing the sample), and finally the capillary was allowed to equilibrate at the final temperature for 30 min before measurement. Afterwards, the bath was left to cool to 24 °C and the sample was tested again to investigate the reversibility of the effect of temperature on measured viscosities. Only guar gum solutions up to a concentration of less than 1 g/L were tested since more concentrated solutions (>1.5 g/L) gave a measurably non-Newtonian response, as determined with the use of a Haake rotational viscometer. The tested polymer concentration range also falls well below the limit $c \approx 4/[\eta]$ ($[\eta]$ – intrinsic viscosity) sometimes given as the onset of entanglement formation for polysaccharides (Robinson, Ross-Murphy, & Morris, 1982).

The kinematic viscosity was measured by allowing each solution to flow under gravity through the capillary. A Lauda PVS1 photo-timing and processing system, interfaced with a computer, was used to automatically measure the flow times from which the kinematic viscosities were calculated. Capillaries of different diameters (from 0.44 to 1.26 mm) were used so that the flow times were between 100 and 200 s. All the measurements were done as triplicates and the average values are reported. In order to find the true viscosities, the densities of all the solutions were also determined at 24 °C as the true viscosity is the product of the kinematic viscosity and density.

One of the simplest ways of assessing interactions between background salts and guar gum is through intrinsic viscosity measurements. The intrinsic viscosity $[\eta]$ is a measure of the inherent ability of a polymer to increase solution viscosity. The most general relationship between intrinsic viscosity and the viscosity of dilute polymer solutions is a power series in concentration and can be given as:

$$\eta_{sp}/c = [\eta] + k_1[\eta]^2c + k_2[\eta]^3c^2 + k_3[\eta]^4c^3 + \dots \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, η_{sp} is the specific viscosity ($\eta_{rel} - 1$, and η_{rel} is the relative viscosity – the viscosity of solution divided by the viscosity of the solvent), and k_i are dimensionless constants. Since η_{sp}/c is the reduced viscosity, η_{red} , which at $c \rightarrow 0$ becomes the intrinsic viscosity $[\eta]$, the above power series is often truncated to a linear approximation which is best known as the Huggins equation (Huggins, 1942):

$$\eta_{red} = [\eta] + k[\eta]^2c \quad (2)$$

where η_{red} is the reduced viscosity, $[\eta]$ is the intrinsic viscosity [dL/g], k is the Huggins coefficient ($k \approx k_1$), and c is the concentration of the polymer [g/dL].

It can be seen that a plot of $\eta_{red} = f(c)$ should be a straight line with the intercept equal to $[\eta]$ and the slope equal to $k[\eta]^2$. Thus, k and $[\eta]$ can graphically be calculated.

Based on experimental observations, the physical meaning of the dimensionless Huggins coefficient k can be summarized as follows (Sakai, 1968a): (a) a polymer exhibits a higher value of k in a poor solvent than in a good solvent, i.e., when the polymer–polymer interactions become favorable over polymer–solvent interactions; (b) it has a value of 0.5–0.7 in a theta solvent; and (c) k is very sensitive to the formation of molecular aggregates.

In other words, the Huggins coefficient k can provide additional information about the state of guar gum macromolecules in various electrolyte solutions, and be a measure of the goodness of the solvent (electrolyte solution).

It should be noted that there are several other empirical equations that can be used to approximately obtain the intrinsic viscosity, or the constant k_1 in Eq. (1), and certain aspects of such alternative treatments of experimental data will be discussed later. All the intrinsic viscosity values given in this study are calculated from the Huggins equation.

2.3. Infrared spectroscopy

In order to characterize the main functional groups on the guar gum macromolecule, Fourier Transform Infrared Spectroscopy (FTIR) was employed and FTIR spectra were recorded with the use of a Perkin–Elmer System 2000 infrared spectrophotometer. A droplet of 1-g/L guar gum solution was first frozen on an AgCl infrared window, then evaporated under vacuum (freeze-dried) and the resulting film of guar gum on the AgCl window was used for infrared analysis. The film preparation procedure was basically that of Rogers and Poling (1978) for polyacrylamides.

3. Results and discussion

Fig. 1a shows FTIR spectra of guar gum films prepared at pH 3 and pH 5.5. The spectra exhibit all typical bands and peaks characteristic of polysaccharides. The 2800–3000 cm^{-1} wavenumber range is associated with the stretching modes of the C–H bonds of methyl groups ($-\text{CH}_3$), the broad band at 3400 cm^{-1} results from the presence of $-\text{OH}$ groups, and the 900–1200 cm^{-1} range represents various vibrations of C–O–C glycosidic and C–O–H bonds.

Of special interest to this investigation is the range between 1500 and 1800 cm^{-1} , typically used to detect the presence of carboxylic groups. It can be seen that there is a small peak on both guar gum spectra at 1640 cm^{-1} (Fig. 1a) which is often assigned to the dissociated carboxylate group ($-\text{COO}^-$). However, the peak does not change its relative position or intensity when the pH is lowered to 3, and no new peak appears near a wavenumber of 1740 cm^{-1} where the protonated COOH group should produce a strong band. The expected shift of the peak at 1640 cm^{-1} towards the 1730–1760 cm^{-1} range can best be illustrated by the data shown in Fig. 1b for two films of

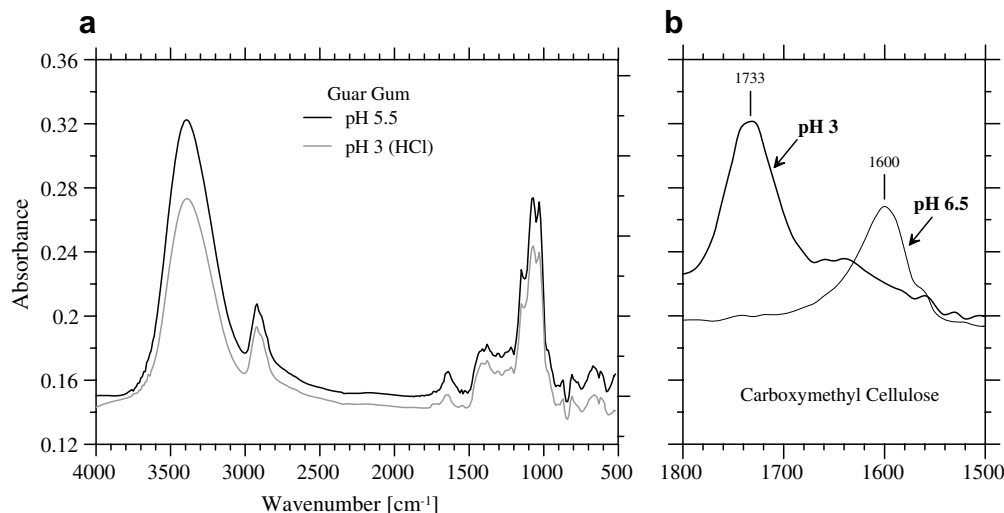


Fig. 1. (a) FTIR spectra of guar gum films prepared at pH 5.5 and pH 3. (b) The effect of pH on the IR absorbance of the carboxylic groups of carboxymethyl cellulose.

carboxymethyl cellulose (MW = 250,000, degree of substitution 0.9, supplied by Polysciences) which were prepared following the same procedure as those of guar gum. Although this effect can be expected to be much more dramatic for carboxymethyl cellulose, due to a high content of carboxylic groups in the cellulose ether, it appears that the KP4000 is free from any residual carboxylic derivatives and can thus be treated as totally non-ionic. Natural gums are known to contain a fraction of uronic derivatives which would impart a weakly anionic character to the guar gum macromolecule (Wang, Ellis, & Ross-Murphy, 2003). It is also worth pointing out that a peak near 1640 cm⁻¹ may originate from in-plane deformations of water molecules hydrogen-bonded to the polysaccharide molecule (Synytsya, Čopíková, Matějka, & Machovič, 2003). Since the KP4000 appears to be non-ionic, any changes in the viscosity of its solutions in the presence of electrolytes cannot originate from changes in the conformation of the macromolecules (coiled vs. extended) resulting from the screening of anionic functional groups by dissolved ions.

Fig. 2 presents the effect of temperature on the viscosity of guar gum solutions in distilled water. The solid lines in Fig. 2 show the Huggins fits to the individual sets of data, except the top line which was averaged over all the points obtained at 24 °C.

It can be seen that there is a marked decrease in the viscosity values when the temperature is raised to 45 °C from 24 °C, and further changes take place when the temperature is raised to 70 °C and 90 °C. More importantly, the effect of temperature is completely reversible. When the same solutions are cooled down to 24 °C, the reduced viscosity values fully “recover” and the data fall on the same line at 24 °C. All individual sets of results follow the Huggins equation very well. It is also quite clear from Fig. 2 that the intrinsic viscosity of guar gum (the intercept of the linear fits at zero guar gum concentration) does not sig-

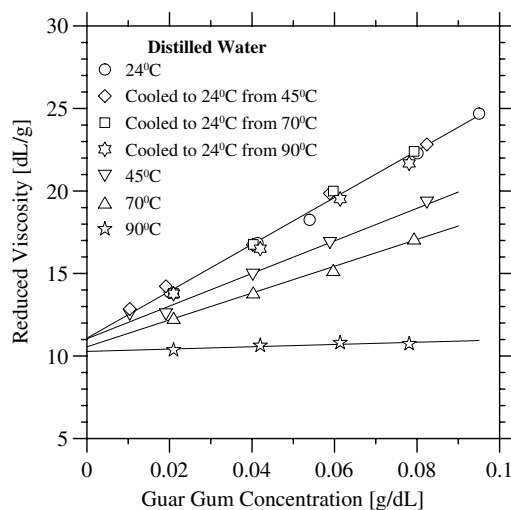


Fig. 2. Reduced viscosity of guar gum solutions in distilled water at various temperatures.

nificantly change with temperature in the studied range – it remains practically the same at 24 and 45 °C, it measurably decreases at 70 °C, and only a minor further decrease can be observed at 90 °C. The average intrinsic viscosity for all the distilled water data, excluding the results at 70 and 90 °C, is 11.0 ± 0.25 dL/g (standard deviation) which is also a good indication of experimental errors involved. The intrinsic viscosity of guar gum is 10.6 dL/g (±0.1 dL/g) at 70 °C and 10.3 dL/g at 90 °C.

Figs. 3–6 show the reduced viscosities of guar gum in alkali metal chloride solutions of varying ionic strength; from that of distilled water to saturation – all at 24 °C. Potassium chloride is the least soluble salt among the tested electrolytes. At 24 °C the concentration of saturated KCl is about 4.1 mol/L. This concentration was therefore the highest concentration at which the effect of the different

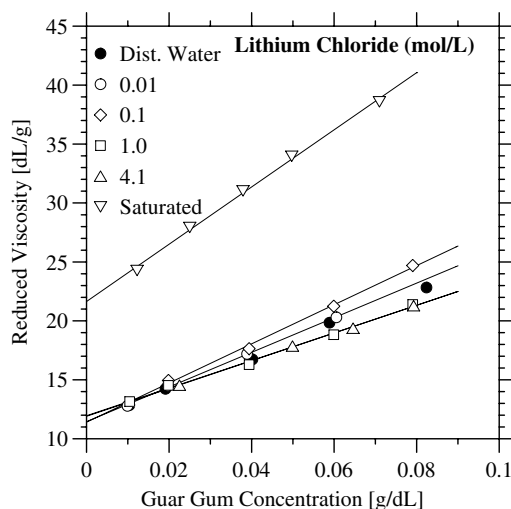


Fig. 3. Effect of lithium chloride on reduced viscosity of guar gum solutions at 24 °C.

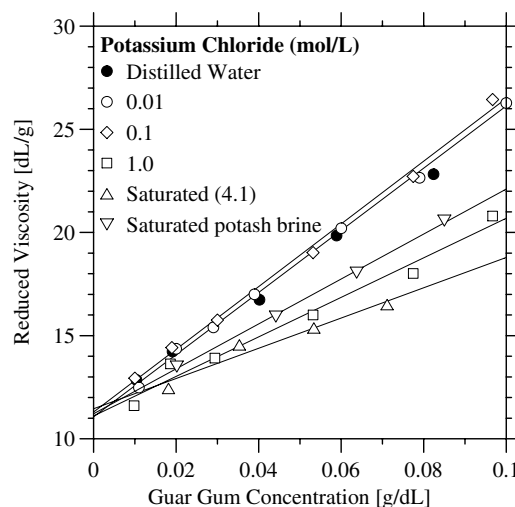


Fig. 5. Effect of potassium chloride on reduced viscosity of guar gum solutions at 24 °C. A set of data for saturated potash brine is also shown.

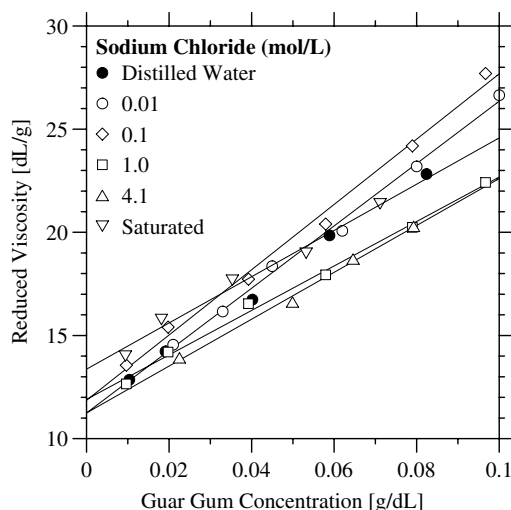


Fig. 4. Effect of sodium chloride on reduced viscosity of guar gum solutions at 24 °C.

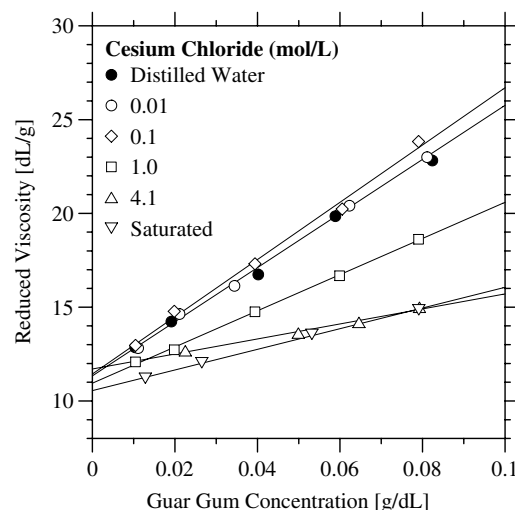


Fig. 6. Effect of cesium chloride on reduced viscosity of guar gum solutions at 24 °C.

salts could directly be compared. The concentrations of saturated LiCl, NaCl, and CsCl solutions are about 13.3, 5.3, and 7.5 mol/L, respectively.

As Fig. 3 illustrates, lithium chloride solutions do not affect the intrinsic viscosity of guar gum up to a salt concentration of 4.1 mol/L (average intrinsic viscosity: 11.7 ± 0.25 dL/g). Only a saturated solution of LiCl gives an intrinsic viscosity value of 21.7 dL/g – the highest value among the tested electrolytes (and urea).

As seen from Fig. 4, the effect of sodium chloride is similar and only a saturated NaCl solution gives a significantly higher intrinsic viscosity (13.4 dL/g), but not nearly as high as that obtained in saturated LiCl. The other NaCl concentrations produce very similar intrinsic viscosity values with an average of 11.6 ± 0.35 dL/g.

Figs. 5 and 6 present the reduced viscosities of guar gum in potassium and cesium chloride solutions, respectively.

Both salts gave qualitatively similar results. Even for highly concentrated KCl and CsCl solutions, the intrinsic viscosities are almost the same as those obtained in distilled water. The average intrinsic viscosity of guar gum in both potassium and cesium chlorides is 11.2 dL/g (± 0.25 dL/g in KCl, and ± 0.3 dL/g in CsCl). One set of data seems to fall outside the statistically significant range; that for saturated CsCl solution for which the intrinsic viscosity is 10.6 dL/g.

Although there appears to be a trend in the average values of intrinsic viscosity in the different electrolytes: 11.7 dL/g for LiCl, 11.6 dL/g for NaCl, 11.2 dL/g for KCl and CsCl, and 11.0 dL/g for distilled water at 24 °C (which may be quite interesting in the context of the subsequent discussion), considering the experimental errors involved these small differences are not quite statistically significant. Therefore, the results for all the salt concentrations (<4.1 mol/L) and distilled water suggest that the

intrinsic viscosity of guar gum is essentially constant over a very wide range of ionic strengths, and only saturated solutions of LiCl, NaCl, and CsCl give a significant effect. Excluding the three saturated solutions, the average intrinsic viscosity of guar gum for all the electrolyte data is 11.3 ± 0.35 dL/g (3%).

Urea gave rather unexpected results, as shown in Fig. 7. Up to a urea concentration of 1 mol/L, the intrinsic viscosity of guar gum remained largely unaffected compared to the value obtained in the salt solutions and distilled water. A 4-M urea solution produced an intrinsic viscosity of 14.5 dL/g, while a saturated solution of urea gave a value of 12.5 dL/g. Interestingly, all guar gum solutions regardless of urea concentration generally yielded viscosities higher than the viscosity of guar gum solutions in distilled water.

As far as other methods of evaluating the raw viscosity data are concerned, several linear approximations were also tested and compared against the Huggins equation, i.e., the Schulz–Blaschke equation ($1/\eta_{\text{red}} = 1/[\eta] - k_{\text{SBC}}c$), the Kraemer equation ($\ln(\eta_{\text{rel}})/c = [\eta] + k_K[\eta]^2c$), and the Martin equation ($\ln(\eta_{\text{sp}}/c) = \ln([\eta]) + k_M[\eta]c$), where the k_i coefficients denote the corresponding dimensionless constants. Since the main focus of this study is on reporting relative changes in $[\eta]$ and k rather than on obtaining the true absolute values, only a qualitative summary of the different approaches is provided. In general, all three equations gave higher intrinsic viscosities compared to those obtained from the Huggins equation. In the worst case – the Huggins and Schulz–Blaschke fits to the 0.1 mol/L LiCl data (Fig. 3) – the difference between the extrapolated intrinsic viscosities was 12% in the studied polymer concentration range. There were also sets of data that gave an excellent agreement (within 2%) between intrinsic viscosities regardless of the method used, e.g., the data obtained in saturated salt solutions (even for saturated LiCl). In fact, it can mathematically be demonstrated that for a set of results that follow the Huggins equation, as all our data

do, the three alternative equations will consistently overestimate intrinsic viscosity compared to the value obtained with the Huggins equation, and the difference will depend on the Huggins constant (Bohdanecký & Kovář, 1982; Lovell, 1989; Sakai, 1968b). For data characterized by a high Huggins coefficient (>0.6 – 0.7), the plotted relationships between $1/\eta_{\text{red}}$ (Schulz–Blaschke), $\ln(\eta_{\text{rel}})/c$ (Kraemer), and $\ln(\eta_{\text{sp}}/c)$ (Martin) and polymer concentration, c , actually give quite non-linear results even when relative viscosity, η_{rel} , is less than 2 ($c \lesssim 0.05$ g/dL in our data). On the other hand, when k values are lower than 0.5 the plotted quantities become linear functions of c , and the agreement between the different methods of data treatment is very good. Our data show exactly such trends but because of the nature of our results (i.e., conversion on the same intrinsic viscosity value) other functions are not shown for clarity.

Since the intrinsic viscosity of guar gum is essentially constant (except saturated LiCl, NaCl, CsCl, and more concentrated urea), the observed differences in the reduced viscosity values in alkali metal chloride solutions, and in more dilute urea, are primarily due to changes in the Huggins coefficient, k (calculated using the slopes and intrinsic viscosities from Eq. (2)). The “anomalous” data for 4-M urea, saturated urea, and saturated LiCl, NaCl, and CsCl are summarized in Table 1.

Huggins constants calculated with the use of Eq. (2) are plotted in Fig. 8 as a function of electrolyte concentration.

It is important to note that the results shown in Fig. 8 reflect changes in the Huggins coefficient under the conditions of *nearly constant* intrinsic viscosity. The intrinsic viscosity can be treated as a measure of molecular size in solution, and is often related to the molecular weight of guar gum through a Mark–Houwink-type of equation (Robinson et al., 1982). Based on the exponent value of the Mark–Houwink equation and the calculated intrinsic chain flexibility, Robinson et al. (1982) concluded that guar gum behaves as a “slightly stiffened” random coil in aqueous solutions – a conclusion that was reinforced by a recent analysis of Picout, Ross-Murphy, Jumel, and Harding (2002).

It should also be recognized that the solution preparation procedure employed in this study does not guarantee that the resulting solutions are truly molecular. Most likely, and based on the study of Picout et al. (2001), the tested guar gum solutions contained a small amount of undissolved guar gum aggregates. The k values in distilled water (Fig. 8) at 24 °C are very high and are certainly consistent with the presence of aggregates (Bohdanecký & Kovář, 1982). According to Sakai’s calculations (Sakai, 1968a) k values in theta solvents can be as high as 1.86 depending on the shape and volume factors of aggregates, with the highest values corresponding to ellipsoid or capsule-like shapes.

The Huggins constant for guar gum in distilled water decreases from 1.07 at 24 °C to 0.73 (± 0.02) at both 45 and 70 °C, and to only 0.07 at 90 °C. In this context, it is

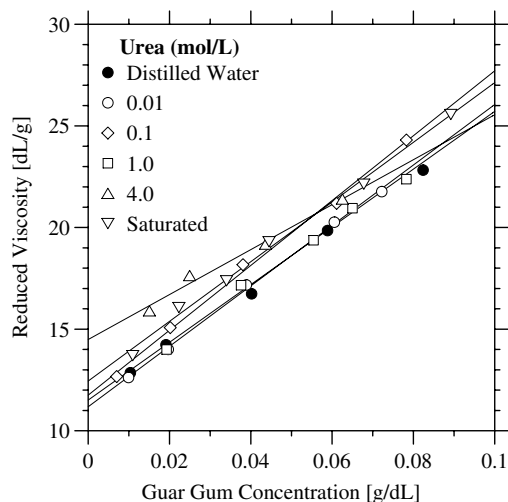


Fig. 7. Effect of urea on reduced viscosity of guar gum solutions at 24 °C.

Table 1
Huggins constants and intrinsic viscosities of guar gum in concentrated urea and saturated NaCl, LiCl, and CsCl solutions

Solution	Intrinsic viscosity [η] (dL/g)	Huggins constant (k)
Urea (4 mol/L)	14.5	0.53
Urea (saturated)	12.5	0.95
NaCl (saturated)	13.4	0.63
LiCl (saturated)	21.7	0.52
CsCl (saturated)	10.6	0.50

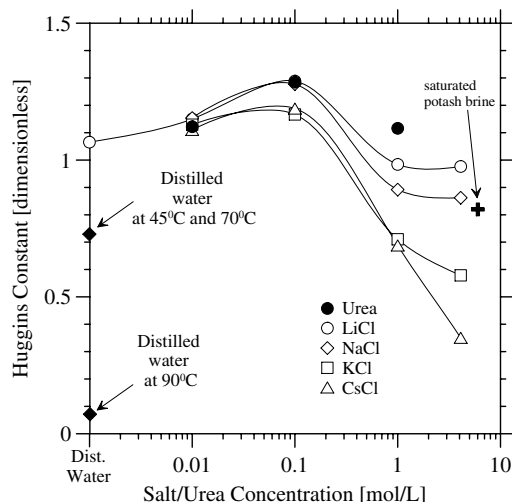


Fig. 8. Effect of electrolyte/urea concentration on Huggins constants of guar gum ($T = 24\text{ }^{\circ}\text{C}$).

interesting to observe that the Huggins constant of the KP4000 guar gum at 45 and 70 $^{\circ}\text{C}$ (0.73) appears to be very close (as far as visual analysis of published data permits) to the Huggins constant obtained by Picout et al. (2001) for a guar solution prepared under conditions described by those authors as “best dissolution conditions”, i.e., producing a truly molecular solution. This particular sample (treated for 10 min at 130 $^{\circ}\text{C}$ under 12-bar pressure) was also characterized by an intrinsic viscosity of ~ 11.3 dL/g (Huggins fit) which is very close to the intrinsic viscosity of the KP4000 in distilled water (11.0 dL/g). It should also be noted that although high pressures and temperatures were employed by those authors in preparing molecular solutions, the actual viscosity measurements were performed at 25 $^{\circ}\text{C}$. Therefore, it should be pointed out that truly molecular solutions of guar gum do not necessarily give low k values (<0.75).

It is worthwhile stressing that the usually accepted values of k for polymers in theta solvents (0.5–0.8) are applicable to flexible chain polymers, and there is both experimental and modeling evidence to suggest that galactomannan chains with a mannose-to-galactose ratio of 2:1 are rather stiff (Petkowicz, Reicher, & Mazeau, 1998; Picout et al., 2001, 2002; Robinson et al., 1982). In other words, it is highly unlikely that guar gum chains in dilute solutions form significant intramolecular bonds and change their overall conformation as the solvent power changes.

Such a collapse of a chain would inevitably result in a large decrease of intrinsic viscosity values but as our data show the intrinsic viscosity of the KP4000 is not strongly affected, and only a small decrease can be detected at temperatures higher than 70 $^{\circ}\text{C}$. At the same time, however, a dramatic change in the Huggins constant can be observed and this decrease can be attributed to the disappearance/dissolution of the colloidal aggregates of guar gum at higher temperatures.

The fact that the intrinsic viscosity of guar gum is quite constant over the studied temperature range does not exclude the possibility of the presence of colloidal guar particles since the contribution of such aggregates to the overall intrinsic viscosity value is very small (Kratochvíl, 1972), and thus the intrinsic viscosity alone is not an accurate measure of the extent of guar gum dissolution (Robinson et al., 1982). The idea that the observed trends in the Huggins constant are due to the enhanced solubility of guar gum aggregates is indirectly supported by the data obtained at 70 and 90 $^{\circ}\text{C}$. As seen from Fig. 2, the intrinsic viscosity of the KP4000 in distilled water is slightly lowered at high temperatures compared to 24 $^{\circ}\text{C}$. As discussed by Picout et al. (2001), this relatively small decrease of the intrinsic viscosity could be interpreted as “the ideal result” in the preparation of truly molecular solutions. Since polymer aggregates can be treated as having very high molecular weights (and light scattering methods certainly sense this effect), in such an “ideal” case, the complete dissolution of the aggregates should lead to a small, measurable decrease in the intrinsic viscosity which in a sense would be equivalent to the disappearance of these apparently high molecular weight fractions.

Since the effect of temperature on the viscosity of guar gum in distilled water is reversible it would be very hard to argue that the observed decrease in the viscosity of guar gum solutions at higher temperature could result from depolymerization of the polysaccharide.

The effect of increasing salt concentration is remarkably similar to the effect of increasing temperature. Assuming that high temperatures promote the dissolution of aggregates, the effect of salts can also be analyzed in terms of their ability to either promote or inhibit the dissolution of colloidal guar gum aggregates by following changes in the Huggins constant, k .

One of the most interesting features of the data presented in Fig. 8 is the maximum on the curves at 0.1 mol/L salts. Dilute salts (<0.1 mol/L) have a tendency to promote the formation of guar aggregates but no detectable differences can be seen between individual electrolytes. The maximum on the curve at an electrolyte concentration of 0.1 mol/L can qualitatively be predicted by a model of the viscosity of polymer solution proposed by Peterson and Fixman (1963). The important assumptions of the Peterson–Fixman model that lead to the appearance of a maximum value of k are that polymer molecules are allowed to form ellipsoid-shaped aggregates, and that aggregates move as rigid bodies in a shear field. In order to reconcile

the data in Fig. 8 with the model one would also need to assume that distilled water at room temperature (24 °C) is a theta-solvent (or a nearly theta-solvent) for guar gum, and that the solvent power (goodness) increases with salt concentration. The results in Fig. 8 certainly suggest that warm distilled water is indeed a better solvent than cold distilled water, and that concentrated salt solutions generally reduce the Huggins constant consistent with increasing solvent power. Therefore, the k value in distilled water at 24 °C (1.07) seems to be in-line with the earlier mentioned calculations of k for differently shaped aggregates in theta solvents (Sakai, 1968a) and the initial increase of k with salt concentration could also result from changes in the shape of the aggregates under the flow conditions.

Interestingly, the model of Peterson and Fixman was criticized for the predicted maximum value of k , which was in contrast to a broad range of known experimental data, and to our knowledge the results presented in this study are the first to show such a maximum.

In the low salt concentration range, guar gum remains in an aggregated state regardless of the solute type. However, as the electrolyte concentration increases above 0.1 mol/L, alkali metal chlorides not only start decreasing the Huggins coefficient but also clear differences between the salts can be observed. Interestingly, LiCl and NaCl appear to approach a limiting k value (0.98 for LiCl and 0.86 for NaCl), while KCl and CsCl continuously reduce the Huggins coefficient to such values that the polymer is effectively under much better solvent conditions in these salts in comparison to distilled water or NaCl and LiCl solutions. A 4.1-M CsCl solution gives a k value of only 0.35 implying that 4.1-M CsCl is a very powerful solvent for guar gum. Recalling that all these changes in the Huggins coefficient take place under constant intrinsic viscosity, it seems that the apparent transition from a poor solvent (distilled water, LiCl and NaCl solutions) to a good solvent (warm distilled water, 4.1-M KCl and CsCl) is associated with the dissolution of colloidal guar gum aggregates. Only saturated CsCl slightly reduces the intrinsic viscosity of guar gum which is again consistent with the “ideal dissolution conditions”, as described by Picout et al. (2001).

Comparing the final k values in 4.1-M solutions of all the salts, the following clear trend can be noted; LiCl gives the highest k value, then NaCl, KCl, and finally CsCl. This observation suggests that the dissolution of guar gum aggregates is much more favorable in KCl or CsCl than in LiCl and NaCl.

The order of the salts in their ability to enhance the solubility of guar gum is actually very significant. Sodium and lithium cations are known to be strongly kosmotropic ions, while potassium and cesium are very strong chaotropes. The terms “kosmotropes” and “chaotropes” refer to ions that are capable of either “reinforcing” or breaking the hydrogen-bonded network of water molecules. Kosmotropes are usually small (in terms of crystallographic radii), strongly hydrated ions, while chaotropes are relatively

large and poorly hydrated. Therefore, kosmotropic ions are also called water structure making ions, and chaotropes are referred to as water-structure breaking ions. It is noteworthy that one of the simplest ways of assessing whether an electrolyte is of chaotropic or kosmotropic nature is through viscosity measurements. As the salt concentration in solution gradually increases, the viscosity of the solution will increase for kosmotropic ions, and it will slightly decrease (compared to the viscosity of pure water) for chaotropes. Chloride anions are usually classified as weakly chaotropic (Wiggins, 2002), and in metal chloride solutions it is usually the cation that determines the “net” behavior of the salt. Thus NaCl and LiCl continuously increase the viscosity of aqueous solutions (LiCl more than NaCl), while the viscosities of KCl and CsCl solutions go through a shallow minimum (corresponding roughly to 90% of the viscosity of pure water) before increasing again near saturation.

At electrolyte (and urea) concentrations higher than 4.1 mol/L, the intrinsic viscosity changes as well, so these highly concentrated solutions should be treated separately. The significantly higher values of the intrinsic viscosity of guar gum (Table 1) indicate that a different type of guar gum structure forms in these systems in comparison to the “simple” aggregates. It should be stressed that such a direct comparison of the saturated solutions is not entirely correct since their molar concentrations are quite different. Nevertheless, it seems that only saturated solutions of the kosmotropic cations (Na and Li) can result in an increase of the intrinsic viscosity above the average value obtained for more dilute electrolytes (≤ 4.1 mol/L). The presence of large amounts of these strongly hydrated ions in guar gum solutions must lead to competitive hydration effects between the ions and the polysaccharide. Hence, it is reasonable to postulate that Li and Na cations extensively bind water molecules into their hydration sheaths leaving no free water molecules to hydrate/solubilize the polymer chain in saturated salt solutions. Under these conditions, strong polymer–polymer interactions are much more favorable than polymer–solvent (water) interactions and the strongly “dehydrated” guar gum undergoes an even further, more extensive networking/aggregation than in more dilute salt solutions. The dehydrated polysaccharide chains must aggregate to adjust to these new solvent conditions, i.e., to the lack of free solvent molecules. The resulting new aggregated structures are characterized by higher intrinsic viscosities than those measured in distilled water or in more dilute salt solutions. It should also be noted that this transition to a more aggregated state at very high salt concentrations is accompanied by a decrease of the Huggins constant for both LiCl and NaCl (Fig. 8 and Table 1). In the case of saturated salt solutions, however, it would probably be more appropriate to refer to these solutions as good solvents for those new types of structures, appearing only in saturated solutions, rather than for the hydrated “simple” guar gum aggregates.

In contrast to Na^+ and Li^+ cations, poorly hydrated K^+ and Cs^+ ions do not strongly interfere with the hydration process of the polymer and allow guar gum to freely interact with water molecules. Therefore, concentrated KCl and CsCl solutions are more powerful solvents for guar gum than NaCl and LiCl.

Considering the above, the effect of urea on the viscosity of guar gum is much more similar to the action of kosmotropic NaCl and LiCl than to the effect of KCl and CsCl. As the urea concentration increases above 1 mol/L, the Huggins constant appears to go through a minimum at 4 mol/L (Table 1 and Fig. 8). At the same time, however, the intrinsic viscosity of guar gum in 4-M urea – the concentration that is often used to destroy extensive polysaccharide structures in more concentrated polymer solutions – is the highest of all urea solutions studied, and is much higher than the intrinsic viscosity in 4.1-M salts. This trend again suggests that, as in the case of highly concentrated LiCl and NaCl, guar gum still remains in an aggregated state in 4-M urea although the “goodness” of this type of solvent is quite different from the goodness of distilled water. In some adsorption studies, 4-M urea is also used as a “breaker” of hydrogen bonds between guar gum and mineral surfaces which provides useful information about the mechanism of interactions between the polymer and various minerals (Wang et al., 2005). It is plausible that these aggregate-breaking properties of urea do not manifest themselves in the low guar gum concentration range studied in this work, where the formation of extensive guar gum structures is not as pronounced as in more concentrated polysaccharide solutions. The well-documented fact that more concentrated guar gum solutions are strongly viscoelastic is an excellent macroscopic evidence of the presence of highly interconnected structures whose solution properties could not be probed by our viscosity measurements made on very dilute guar gum solutions. For the KP4000 guar gum, this onset of viscoelasticity appears to be near a polysaccharide concentration of 1.5 g/L, as mentioned in the experimental section.

Finally, the saturated potash brine behaves more like 4.4-M NaCl than 1.7-M KCl (note the composition of the brine given in the experimental section). The brine produces an intrinsic viscosity value of 11.2 dL/g (Fig. 5) and a k value of 0.82. For comparison, the k values are 0.86 and about 0.65 in 4.1-M NaCl and 1.7-M KCl, respectively. Following the above discussion, guar gum appears to be in an aggregated state suggesting that the dehydration of the polymer by the high concentration of Na^+ ions dominates over the structure-breaking capabilities of K^+ in this saturated mixed-electrolyte system.

The similarity between the effect of high temperature and high salt concentrations deserves a couple of additional comments. The main property that is affected in both systems is the *relative* degree of water–water vs. water–guar (polymer hydration) hydrogen bonding which in turn is fundamentally related to the way guar gum dissolves in

aqueous solutions. Both high temperature and chaotropic ions reduce the viscosity of water which is a macroscopic manifestation of the breaking of hydrogen bonds between water molecules. Gittings et al. (2000) analyzed the behavior of guar gum in heavy water (D_2O) and concluded that D_2O is a worse solvent for guar gum compared to H_2O , as suggested by larger guar aggregate sizes measured in D_2O . From our discussion point of view, it should be mentioned that the viscosity of D_2O is about 25% higher than that of H_2O at 25 °C (Horita & Cole, 2004), and D_2O should form stronger hydrogen bonds than H_2O (Chen, Ivanov, Klein, & Parrinello, 2003).

Although direct light scattering measurements would be needed to confirm the dissolution of aggregates in chaotropic salt solutions (KCl and CsCl), our results highlight the importance of background ions in controlling polymer hydration phenomena and defining the behavior of guar gum in dilute and concentrated electrolyte solutions.

From the adsorption point of view, the presence or dissolution of colloidal guar gum aggregates, as influenced by various background salts, should lead to different modes of polymer adsorption on mineral surfaces. Traditionally, it is assumed that individual guar gum molecules participate in the adsorption process from dilute guar gum solutions, but as the results suggest it is probably more accurate to consider the adsorption of entire guar gum aggregates as opposed to single polymer chains.

4. Conclusions

The intrinsic viscosity of the KP4000 guar gum is remarkably constant over a wide range of alkali metal chloride concentrations at 24 °C. No effect of the salts on the intrinsic viscosity can be detected up to an electrolyte concentration of 4.1 mol/L. The average intrinsic viscosity under these conditions is 11.3 dL/g ($\pm 3.0\%$). A simple analysis of changes in the Huggins coefficient indicates that guar gum chains are in an aggregated state in distilled water and in dilute salt solutions. At higher electrolyte concentrations (≥ 0.1 mol/L), the state of the aggregation of the polysaccharide depends on the kosmotropic or chaotropic properties of the background electrolytes. The presence of strongly chaotropic ions, such as K^+ and Cs^+ , (water-structure breaking ions) seems to induce the dissolution of guar gum aggregates into individual molecules. Kosmotropic ions, such as Li^+ and Na^+ , affect guar solutions differently and these strongly hydrated ions effectively decrease the amount of free water molecules in solution that would otherwise be available for polymer chain solubilization. As a result, guar gum chains undergo an even more extensive aggregation in saturated solutions of LiCl and NaCl to form larger structures characterized by significantly higher intrinsic viscosities. Overall, concentrated chaotropic electrolyte solutions are very powerful solvents for guar gum.

The effect of urea on the properties of dilute solutions of the KP4000 guar gum is comparable to the effect of NaCl.

Therefore, the “dispersing” capabilities of urea towards guar gum aggregates appear to be very poor in the studied polymer concentration range.

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