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Viscometric and transmitted light investigation of agarose and agarose-guar water systems

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Summary

Agarose water solutions of different concentrations and agarose-guar water solutions of 1% (w/w) total concentration and varied compositions were submitted to viscometric and turbidimetric measurements as function of the temperature. Phase diagrams for both systems are compared. For agarose solutions, phase separation occurs prior to gelation within a certain concentration range, and network formation seems to take place by the connectivity of the polymer-rich domains. For the mixed agarose-guar system, the homogeneous solutions gel directly.

Introduction

Multicomponent systems have recently been attracting much interest. In biopolymer systems, the possibility of improving rheological characteristics at low cost has focused attention to polysaccharide mixtures, in which synergistic effects have been observed.

In general, galactomannans are used as one of the components of such mixtures. The other component may be a gelling or a non gelling polysaccharide. The latter case may be exemplified by gel formation when the non-gelling xanthan is mixed to galactomannans[1-4].

For synthetic polymers, some models have been proposed to explain the sol-gel transition in covalently crosslinked networks [5,6] and in those formed by extensive entanglements [7,8]. In the case of polysaccharide systems, several techniques have been applied to the investigation of thermoreversible gels[9-13], but this subject is still under discussion[14].

In this work, agarose-water and agarose-guar-water gelling systems are studied. Agarose consists of alternating (1→3)-β-D-galactopyranosyl and (1→4)-3,6-anhydro-α-L-galactopyranosyl repeat units. Guar galactomannan is a non gelling polysaccharide in which the (1→4)-β-D-mannan backbone is substituted to a high extent of (1→6)-α-D-galactopyranosyl units. Agarose and agarose-guar water solutions were submitted to viscometric and transmitted light experiments during slow cooling from 50 to 8°C, to obtain comparative information about gelation in both systems.

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Experimental

Agarose, supplied by Cialgas, Companhia Industrial de Algas, was used as received. The intrinsic viscosity, $[\eta]$ = 3.24 dl/g, was determined in a Ostwald type viscometer in 0.75 M NaSCN, at 35°C. The viscosity average molecular weight, $\overline{M}_v$ = 1.23 x 10^5, was calculated according to the Mark-Houwink relationship, taking the K = 0.07 and a = 0.72 values from the literature[15].

Guar gum, purchased from The Dow Chemical Company, was dissolved overnight in water at room temperature. This solution was filtered through 3.0 and 0.8 μm membranes. The product was recovered as a precipitate by addition of ethyl alcohol, and dried under vacuum. The intrinsic viscosity, $[\eta]$ = 13.6 dl/g, was determined in the same viscometer in water, at 25°C. The viscosity average molecular weight, $\overline{M}_v$ = 1.99 x 10^6, was calculated as before, by using K = 3.8 x 10^{-4} and a = 0.723 values[16].

Agarose solutions were prepared by dispersion in water at room temperature, followed by heating at 70°C for 30 minutes and at 100°C for 15 minutes. Guar gum solutions were prepared by stirring the water dispersion at room temperature overnight. Agarose-guar water solutions at 1% w/w total concentration were obtained by appropiate mixture of the pure gums solutions at 85°C. The hot mixed solutions were poured into a viscometric or optical thermostated cell and maintained at 50°C for 15 minutes before beginning the measurements.

The critical temperatures of gelation, T_c, were determined by the slow cooling of the solutions (0.4°C/min) placed in a Small Sample Adapter SC4-31/13R of a Brookfield Synchro-Lectric LVT viscometer, and measuring the apparent viscosity with a spindle number 31, at 0.1 s^{-1} shear rate.

Transmitted light as function of the temperature was measured by a silicon photodetector (Centralab, model CSC-12), connected to an ECB multimeter, model MDM 220, after passing through the solution. The light source was a 2mW He-Ne laser beam, which was expanded to avoid local heating of the material. The samples were placed in an optical window vacuum cryostat, in order to prevent light scattering due to water condensation in the cell. Starting from 50°C, the temperature was decreased (0.4°C/min) and regulated by means of a copper-constantan thermocouple. A Keithley multimeter, model 177, was used to monitor the sample temperatures.

Results and Discussion

Guar solutions exhibit very high viscosities and this fact limited the experiments to a maximum of 1% w/w concentration. Otherwise, the low viscosity of agarose solutions was not accurately measured by the available equipment, under the initial experimental conditions (50°C); it was necessary to fix the lowest agarose solution concentration at 0.4% w/w, even though gel formation has been visually observed from 0.1% w/w. Apparent viscosity data for agarose solutions were taken as the temperature was diminished from 50 to 8°C. A remarkable increase in viscosity pointed out the critical temperature

at 0.1 s^{-1} shear rate, as the average temperature between the first one at which viscosity could be detected accurately and the last one at which no reproducible viscosity measurement was possible.

Figure 1 shows the non linear increase in the apparent viscosity of agarose solutions, obtained by lowering the temperature. As expected, the critical temperature of gelation shifted to higher values with the increase in concentration.

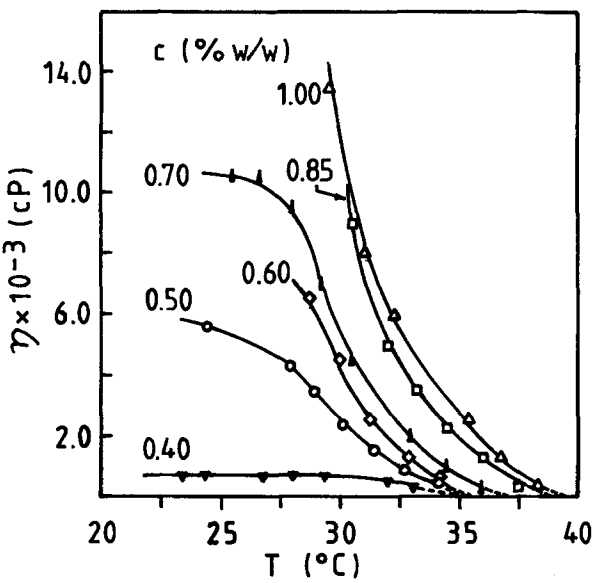

Figure 1- Apparent viscosity as a function of temperature for agarose solutions of different concentrations.

The decay of the transmitted light intensity observed for agarose solutions with decreasing temperaturests is shown in Figure 2(a-b). The curves showed the same features: in the initial part of the experiment (50-40°C), the transmitted light intensity, I/I_o, remained constant. Further cooling caused a sharp decrease in I/I_o. The cloud point was taken as the intersection of these two regions. Finally, the third region was reached, whose extension seems to depend on concentration. The higher the concentration, the earlier the levelling off of the third region was reached. The nature of this region may be due to the completion of phase separation[17].

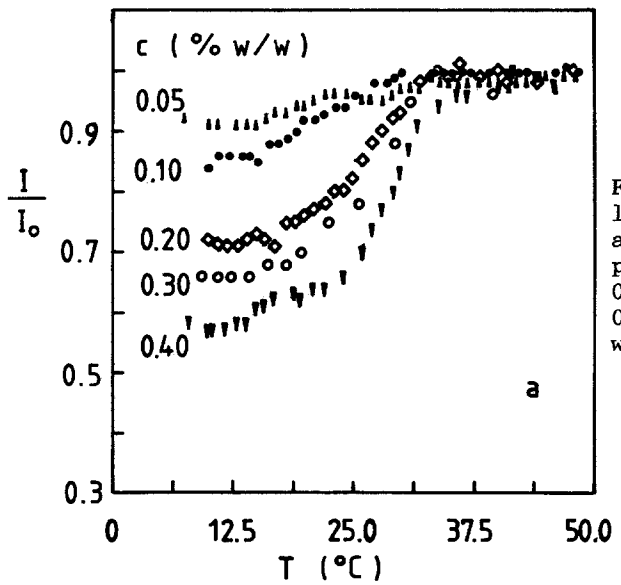

Figure 2a- Transmitted light intensity as a function of temperature for 0.05 , 0.10 , 0.20 , 0.30 and 0.40 % (w/w) agarose water solutions.

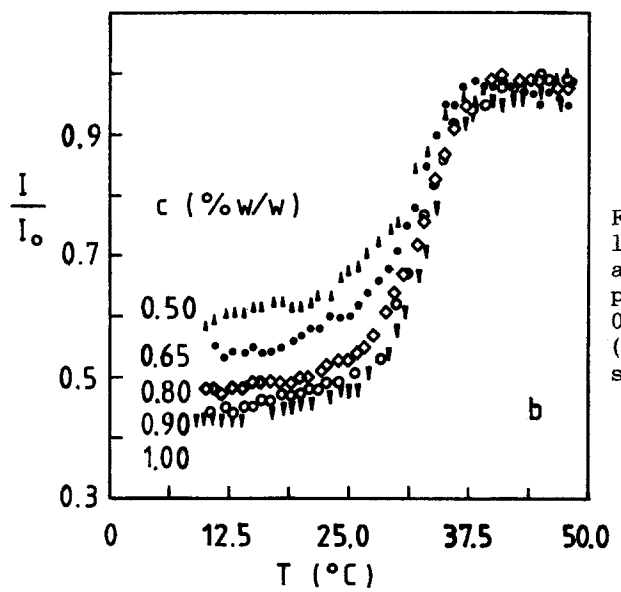

Figure 2b- Transmitted light intensity as a function of temperature for 0.50, 0.65 0.80 , 0.90 and 1.00 % (w/w) agarose water solutions.

The determination of the critical temperature of gelation was more accurate for agarose-guar mixed solutions at 1% w/w total concentration, as shown in Figure 3 (a-b). The decrease in the temperature from 50°C caused a clear discontinuity in the viscosity behaviour. As may be noticed, the T_c values underwent a shift to higher temperatures as the agarose composition increased in the mixture.

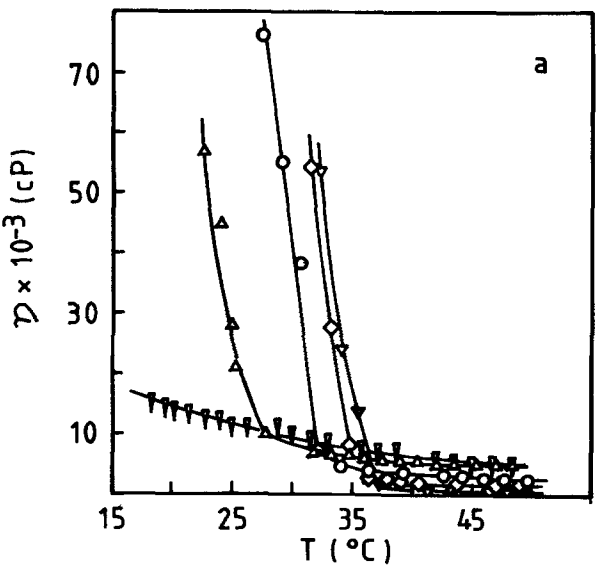

Figure 3a- Apparent viscosity as a function of temperature for mixed agarose-guar solutions of different compositions: (△) 0.1: 0.9 , (o) 0.2 : 0.8, (◇) 0.3:0.7, (▽) 0.4: 0.6 and (▼) for guar gum at 1% (w/w) total concentration.

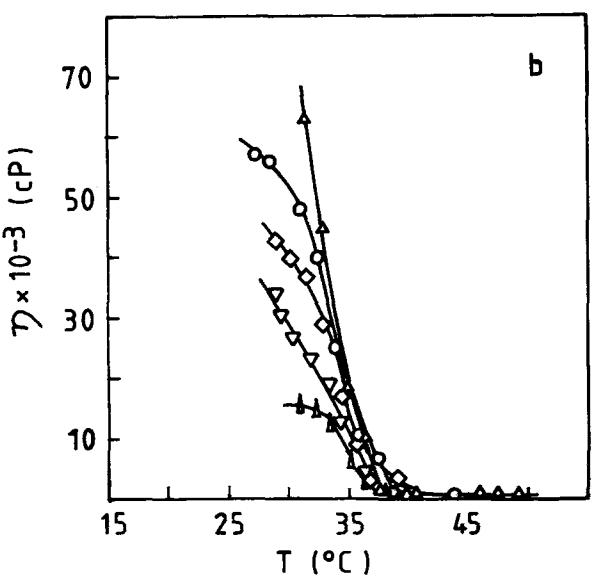

Figure 3b- Apparent viscosity as a function of temperature for mixed agarose-guar solutions of different compositions: (△) 0.5: 0.5 , (o) 0.6:0.4, (◇) 0.7:0.3 , (▽) 0.8:0.2 and (▼) 0.9:0.1 at 1 % (w/w) total concentration.

Figure 4 (a-b) shows I/I_o as a function of temperature for agarose-guar solutions. The pure guar solution and the agarose-guar (0.1:0.9 ratio) mixed solutions did not show discontinuity by lowering the temperature, although the last mixed solution exhibited gel formation. Evidence of a discontinuity in I/I_o was observed for the 0.2:0.8 agarose-guar solution and for those with higher compositions in agarose. The curves followed the same pattern as those depicted for agarose solutions in Figure 2.

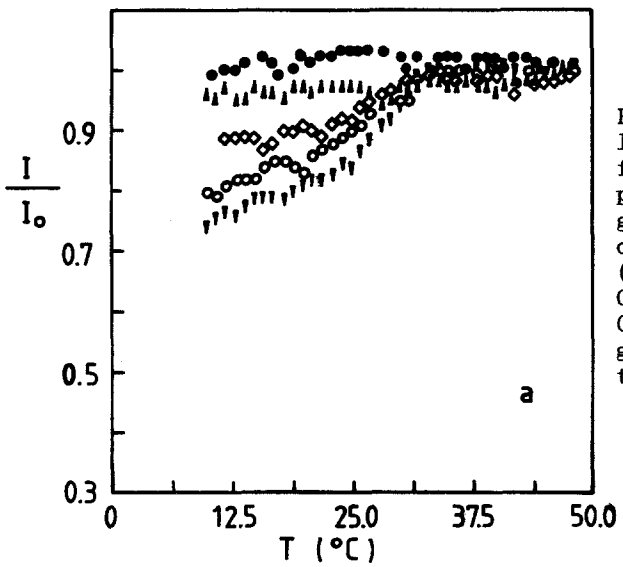

Figure 4a- Transmitted light intensity as a function of temperature for agarose-guar mixed solutions of different compositions: (●) 0.1:0.9 , (◇)0.2:0.8 , (○) 0.3:0.7,(▾) 0.4:0.6 and (▴) for guar gum at 1 % (w/w) total concentration.

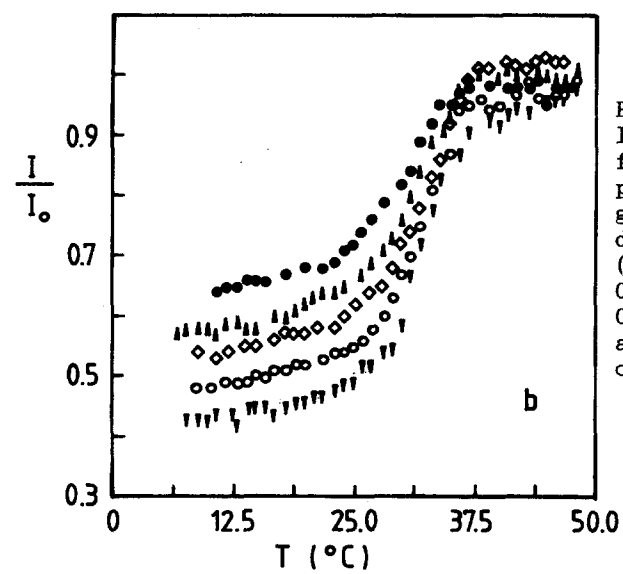

Figure 4b- Transmitted light intensity as a function of temperature for agarose-guar mixed solutions of different compositions: (●) 0:5:0.5 , (▴)0.6:0.4 , (◇) 0.7:0.3,(○) 0.8:0.2 and (▾)0.9:0.1 at 1 % (w/w) total concentration.

The results from viscosity and transmitted light intensity measurements carried out for agarose solutions are collected in the phase diagram of Figure 5. The linear behaviour of T_c vs. c curve was expected, at least in the 0.4-1.0% (w/w) concentration range[18]. The diagram seems to indicate that at low concentrations phase separation occurs before gelation; or that under these conditions network formation occurs by connection of polymer-rich domains. At high concentrations,

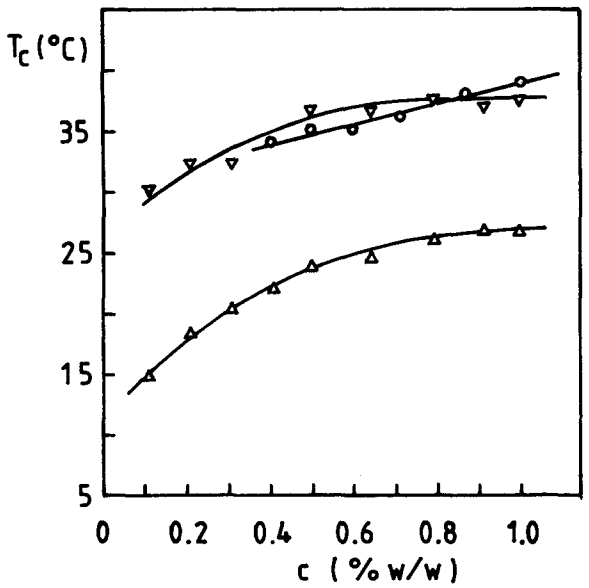

Figure 5- Phase diagram for the agarose-water system : initiation temperatures (▽), apparent completion temperatures (△), and critical temperatures of gelation (o).

there is a tendency for gelation, prior to phase separation. The homogeneous gel would be formed first and the decrease in the temperature would lead to heterogeneous gel, consisting of connected polymer-rich domains and dilute polymer solution.

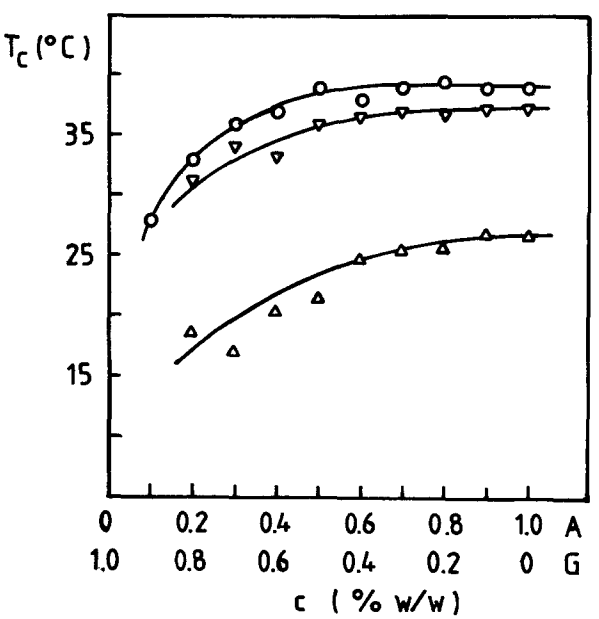

Figure 6- Phase diagram for the agarose-guar-water system: initiation temperatures (▽) apparent completion temperatures (△), and critical temperatures of gelation (o).

Similar conclusion was reached by other authors, after isothermic experiments[19].

The same kind of diagram was composed for agarose-guar mixed solutions and is shown in Figure 6. For this system, the critical temperatures of gelation, T_c, obtained for each one of the studied compositions, are always higher than the cloud points. This means that gel formation occurs without phase separation.

The comparison between the diagrams of Figures 5 and 6 indicates the similarity between the two phase separation curves. It also reveals the dissimilarities in the gelation process. For low concentration agarose-water solutions, phase separation favours gelation. The presence of guar as a third component leads the homogeneous solution directly to gelation, and supports the idea that phase separation is not necessary to gel formation.

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