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Abstract

Rheological measurements on a solution undergoing inverse melting are presented as a function of temperature and concentration. This solution exhibits, under shear, the phenomenon of shear thickening, i.e. an increase of apparent viscosity with increase in shear rate $\dot{\gamma}$. In particular a shear-thickening transition happens at a critical shear rate $\dot{\gamma}_c$ which increases with increasing concentration. It defines two different regimes: at low shear rates $\dot{\gamma} < \dot{\gamma}_c$ the fluid shows Newtonian behaviour, while at shear rates $\dot{\gamma} > \dot{\gamma}_c$ a transition from the Newtonian to the shear-thickening regime is observed. This behaviour is interpreted on the basis of a relaxation process activated by the shear and characterized by a relaxation time $\tau = 1/\dot{\gamma}_c$. In the thickening region the viscosity data are well fitted with a power-law model $\eta(\dot{\gamma}) = A\dot{\gamma}^{n-1}$ with $n = 1.8$. The temperature and concentration behaviour of the zero shear viscosity, the power-law exponent, and the critical shear rate are discussed.

§ 1. Introduction

The study of the rheological properties of complex fluids has gained increasing attention due to the variety of macroscopic behaviours exhibited when they are subjected to shear. Thixotropy and rheopexy are observed respectively when the viscosity decreases or increases with time at constant shear rate, shear thickening or thinning are found when the viscosity increases or decreases with increasing shear rate while shear banding arises from the presence of regions with high and low stresses coexisting in layers. This rich phenomenology [1,2] is the clear expression of the multiple microscopic inter-particle interactions characteristic of the specific system. Therefore the investigation of the rheological properties of many substances provides advances in understanding the relationship between the structure, the dynamics and the flow properties. Many of the singular behaviours described above have been observed in colloidal suspensions, which represent model systems for experimental and theoretical studies. In particular it has been observed that concentrated suspensions of solid particles always show shear thickening [3] if measured in the appropriate shear rate range.

Shear thickening happens when the apparent viscosity of a fluid increases with increasing shear rate. To explain this phenomenon two main theories have been elaborated: one attributes shear thickening to an increase of disorder in the fluid. It implies that a monodisperse suspension of particles makes a discontinuous jump in viscosity at a critical shear rate due to an increasing disorder; this phenomenon was also referred as order-disorder transition [4]. The other one ascribes

1 the increase of the viscosity to the formation of clusters, mechanism driven by shear forces which
2 make the particles to approach each other. In this theory the increase of shear viscosity corresponds
3 to an increase of the cluster size [5].
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7 Recent models for shear thickening in colloidal suspensions [6,7] based on schematic mode
8 coupling theory (MCT) demonstrate that shear thickening can be attributed to a transition from a
9 fluid to a non-ergodic “jammed” state induced by shear. In this model, flow curves representing the
10 stress versus the shear rate exhibit shear thickening and static jam for proper values of the
11 parameters. The idea of considering shear thickening as a driving mechanism for glass transition
12 induced by shear arose from the parallelism with the colloidal glass transition close to which shear
13 thickening is often observed. The effect of shear flow on glass transition has recently been the
14 subject of theoretical [6-11] and experimental [12-13] investigations.
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18 Results similar to those obtained with MCT for shear thickening have been directly derived
19 by Sellitto and Kurchan [14] starting from a spin model for inverse freezing in which a phase re-
20 entrance driven by entropy was predicted [15]. They exploited the analogy between freezing by
21 heating and jamming by stirring to propose a mechanism for shear thickening analogous to the
22 phase re-entrance. From this microscopic approach they obtained a flow curve surprisingly similar
23 to that derived with MCT for thickening.
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27 On the basis of these recent developments we thought to study experimentally the rheological
28 behaviour of a system characterized by inverse melting with the aim to investigate the possible
29 analogy between entropy driven transitions and shear thickening. To this purpose we performed
30 rheological measurements on a solution of α -cyclodextrin (α CD) ($C_{36}H_{60}O_{30}$), water and 4-methyl-
31 piridyne (4MP) (C_6H_7N) known to undergo an inverse melting transition [16-18] for certain values
32 of concentration and temperature. A preliminary result has been reported in reference [17].
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36 We found a non-Newtonian behaviour above a critical shear rate $\dot{\gamma}_c$ and in particular the
37 presence of shear thickening. On the basis of the analogy proposed by Sellitto and Kurchan [14] we
38 interpret shear thickening in these inverse melting solutions as a driving mechanism for the glass
39 transition, although an arrested state is not observed in the investigated shear rate and concentration
40 range.
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44 Here we present such measurements, we discuss the shear viscosity behaviour, we analyze the
45 data and discuss the temperature and concentration dependence of some parameters related to the
46 size of the particles and to the relaxation time of the solution under shear.
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53 § 2. Experimental details

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The solution is composed of liquid 4MP of 98% purity, α CD hydrate both purchased by Aldrich and deionized water. The sample was prepared by dispersing the powder (α CD) in 4MP and water in proper molar ratio and stirring for about 4 hours until the suspensions were cleared. The measurements were performed through a rheometer Reostress RS150 Haake in Couette geometry, it is equipped with two coaxial stainless steel cylinders of which the inner one, the sensor, is fixed to a rotor motor and has a diameter of 2 mm (model Z20DIN). The sample was placed in the 0.85 mm gap between the two cylinders of which the outer one was thermalized through a liquid flux cryostat DC50-K75 Haake. The rheometer was used in control rate (CR) mode to measure the stress change with the applied shear rate.

The measurements were performed as a function of the shear rate $\dot{\gamma}$ in the range 0-1400 s⁻¹, the sample was prepared at seven different concentrations of α CD, water and 4MP with molar ratios 1:6:x respectively with $50 \leq x \leq 200$ and varying the concentration of the solution by varying the amount of 4MP, each concentration was investigated as a function of the temperature in the range 293-340 K.

The shear stress σ and the shear viscosity η of the solution linked through the relation $\sigma(\dot{\gamma}) = \eta(\dot{\gamma})\dot{\gamma}$ have been measured as a function of the shear rate at different temperatures and concentrations. An example of such measurements is shown in Fig.1 where the viscosity is plotted as a function of the shear rate at fixed concentration $c = 84$ mg / ml of α CD in 4MP and at the indicated temperatures.

[Insert figure 1 about here]

§ 3. Results and discussion

Fig.1 displays the general trend of the investigated solutions, they present a shear thickening transition when the shear rate exceeds a critical value $\dot{\gamma}_c$. Many complex fluids have been found to exhibit this behaviour [3, 19-22] and it is generally related to the changes in the microscopic structure of the fluid. The data shown in figure are compared with a $\dot{\gamma}^{0.8}$ power-law behaviour represented by the dashed line.

In Fig. 2 the concentration behaviour of the flow curve is presented and the shear viscosity vs shear rate displayed at fixed temperature (T=293 K) for seven concentrations of α CD in 4MP. For all the concentrations two different regimes are observed: an almost constant shear viscosity for $\dot{\gamma} < \dot{\gamma}_c$ (Newtonian regime) followed at $\dot{\gamma} > \dot{\gamma}_c$ by an increase of shear viscosity at increasing shear rate (shear-thickening regime).

[Insert figure 2 about here]

It is evident that at a given shear rate the value of the viscosity is higher at higher concentrations and the onset of the shear thickening occurs at larger shear rates with the increase of concentration. The more concentrated the solution is the higher the shear has to be in order to observe shear thickening. The data have been analyzed considering the two observed different behaviours of the viscosity in the full investigated shear rate range. For $\dot{\gamma} < \dot{\gamma}_c$ the viscosity is a linear function of the shear rate and often it is shear rate independent. In this region the data have been fitted with:

$$\eta(\dot{\gamma}) = \eta_0 + B\dot{\gamma} \quad \dot{\gamma} < \dot{\gamma}_c$$

For $\dot{\gamma} > \dot{\gamma}_c$ the viscosity increases with shear rate and the data have been fitted with a power law model [3, 8-9, 23-24] in which the stress is expressed as:

$$\sigma(\dot{\gamma}) = A\dot{\gamma}^n$$

and the viscosity, related to the stress through the relation $\eta(\dot{\gamma}) = \sigma(\dot{\gamma})/\dot{\gamma}$, is given by

$$\eta(\dot{\gamma}) = A\dot{\gamma}^{n-1} \quad \dot{\gamma} > \dot{\gamma}_c$$

The fits are shown in Fig. 2. for two concentrations. The parameters of interest here are η_0 , $\alpha=n-1$ and the critical shear rate value which signs the change of the shear viscosity behaviour.

[Insert figure 3 about here]

[Insert figure 4 about here]

Fig. 3 and Fig. 4 display the variation of the zero shear viscosity as a function of the concentration and temperature. It decreases with temperature and increases with concentration in agreement with the physical intuition. In addition in the limit of zero concentration it is compatible with the value of the pure solvent $\eta = 0.94$ mPa s [25] at $T = 293$ K.

[Insert figure 5 about here]

Fig. 5 displays the exponent $\alpha = n-1$ of the power law discussed above. For the most of the concentration $c \leq 125$ mg/ml it is almost temperature and concentration independent and assumes the value $\alpha \approx 0.8$. It gives the scaling of the apparent viscosity as a function of the shear rate. In general the power law fits well data at high shear rates [2] and for $n > 1$ reproduces the behaviour of materials shear thickening like. This is the case of our solutions for which $n \approx 1.8$. For $c = 201$ mg/ml and 172 mg/ml a slight dependence of α with temperature is observed.

[Insert figure 6 about here]

In Fig. 6 the dependence of the critical shear rate as a function of the temperature at different concentrations is shown together with the temperature-concentration phase diagram from ref [17] reported in the inset. The shear measurements have been performed in the low temperature liquid

(LTL) region shown in the phase diagram. The critical shear rate decreases with temperature at fixed concentration while it becomes bigger and bigger at increasing concentration for fixed temperature. According to literature, studies carried on a variety of shear thickening systems, mainly composed of suspensions of solid particles in a fluid, have shown [3] that a general dependence of the critical shear rate on the average particle size (a) exists and in particular that the onset for shear thickening is correlated with $1/a^2$ [3,4] if it is associated to an order-disorder transition in systems with phase volume around 50% while it correlates with $1/a^3$ if particle clustering is activated [4]. In both cases an inverse proportionality with the average size particle is found, this means that systems characterized by small particles would make the shear thickening transition to happen at higher shear rates. On the basis of these observations the results of Fig. 6 would indicate an increase of the “particles size” with temperature at fixed concentration.

In this respect we could speculate that the applied shear favours the breaking of the intra-molecular hydrogen bonds (HB) of α CD at a critical value $\dot{\gamma}_c$ which depends either on concentration and temperature. This in turn could facilitate the reformation of intermolecular HB with water and 4MP molecules giving rise to the formation of more complex aggregations and to an increase of viscosity.

Furthermore one can consider that the applied shear rate induces a relaxation and that the transition of the system at a critical shear rate $\dot{\gamma}_c$ from a dynamical behaviour to another one is characterized by a relaxation time $\tau = 1/\dot{\gamma}_c$ which in turns is bigger at low critical shear rates. This is coherent with the fact that an increase of particle size would imply a slowing down of the dynamics and hence a longer relaxation time. It seems therefore that shear thickening results from a slowing down of the dynamics induced by a shear flow.

§ 4. Conclusions

In conclusion we have investigated the rheological response of molecular solutions of α CD, water and 4MP characterized by inverse melting. Measurements of the flow curves in Couette geometry as a function of the concentration and temperature have been performed. They are characterized by the phenomenon of shear thickening and in particular a critical shear rate $\dot{\gamma}_c$ exists at which a transition between two different regimes is observed. At low shear rates $\dot{\gamma} < \dot{\gamma}_c$ the fluid shows Newtonian behaviour, while at shear rates $\dot{\gamma} > \dot{\gamma}_c$ a transition from the Newtonian to the shear-thickening regime is observed. This behaviour is ascribed to the presence of a relaxation induced by

shear with a characteristic relaxation time defined as $\tau = 1/\dot{\gamma}_c$. In this view shear thickening can be read as the result of a slowing down of the dynamics induced by shear flow.

The connection and the similarities between the investigated inverse melting solutions and the schematic model for shear thickening and entropy driven transitions proposed by Sellitto and Kurchan [14] induces to interpret the observed shear thickening as a driving mechanism for glass transition although a transition to an arrested state is not observed in the investigated shear rate and concentration range.

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Figure captions

Figure 1.

Shear viscosity of α CD-water-4MP solutions as a function of shear rate for different temperatures and at fixed concentration measured in rotational mode as discussed in the text. The dashed dot line

1
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3 is a $\dot{\gamma}^{0.8}$ power-law behaviour. In the inset a log-log plot of the shear thickening region is reported
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5 and the data are compared to the $\dot{\gamma}^{0.8}$ (dashed dot line) and $\dot{\gamma}$ (full line) behaviour.
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10 Figure 2.

11 Shear viscosity of α CD-water-4MP solutions (symbols) as a function of shear rate for different
12 concentrations and at fixed temperature measured in rotational mode. The solid lines are the best
13 fits to the data obtained using the combination of a linear law in the Newtonian regime and a power
14 law for the non-Newtonian region as discussed in the text. The crossing point between the two fits
15 represents the critical shear rate value. In the insets the parameters A and B of the fit functions
16 discussed in the text are shown as a function of the concentration for T = 293 K.
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23
24 Figure 3.

25 Shear viscosity η_0 of α CD-water-4MP solutions in the limit of zero shear rate as a function of
26 temperature for different concentrations.
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31
32 Figure 4.

33 Shear viscosity η_0 of α CD-water-4MP solutions in the limit of zero shear rate as a function of
34 concentration at the indicated temperatures, the dashed line is a guide for the eyes.
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38
39 Figure 5.

40 Parameter α obtained from the fit with the power law as discussed in the text. It is reported as a
41 function of temperature at the indicated concentrations.
42
43
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45
46 Figure 6.

47 Critical shear rate of α CD-water-4MP solutions as a function of temperature for different
48 concentrations. In the inset the temperature-concentration phase diagram [17] obtained via
49 calorimetric [17] and neutron scattering [16] measurements is shown. The shear measurements have
50 been performed in the LTL liquid region.
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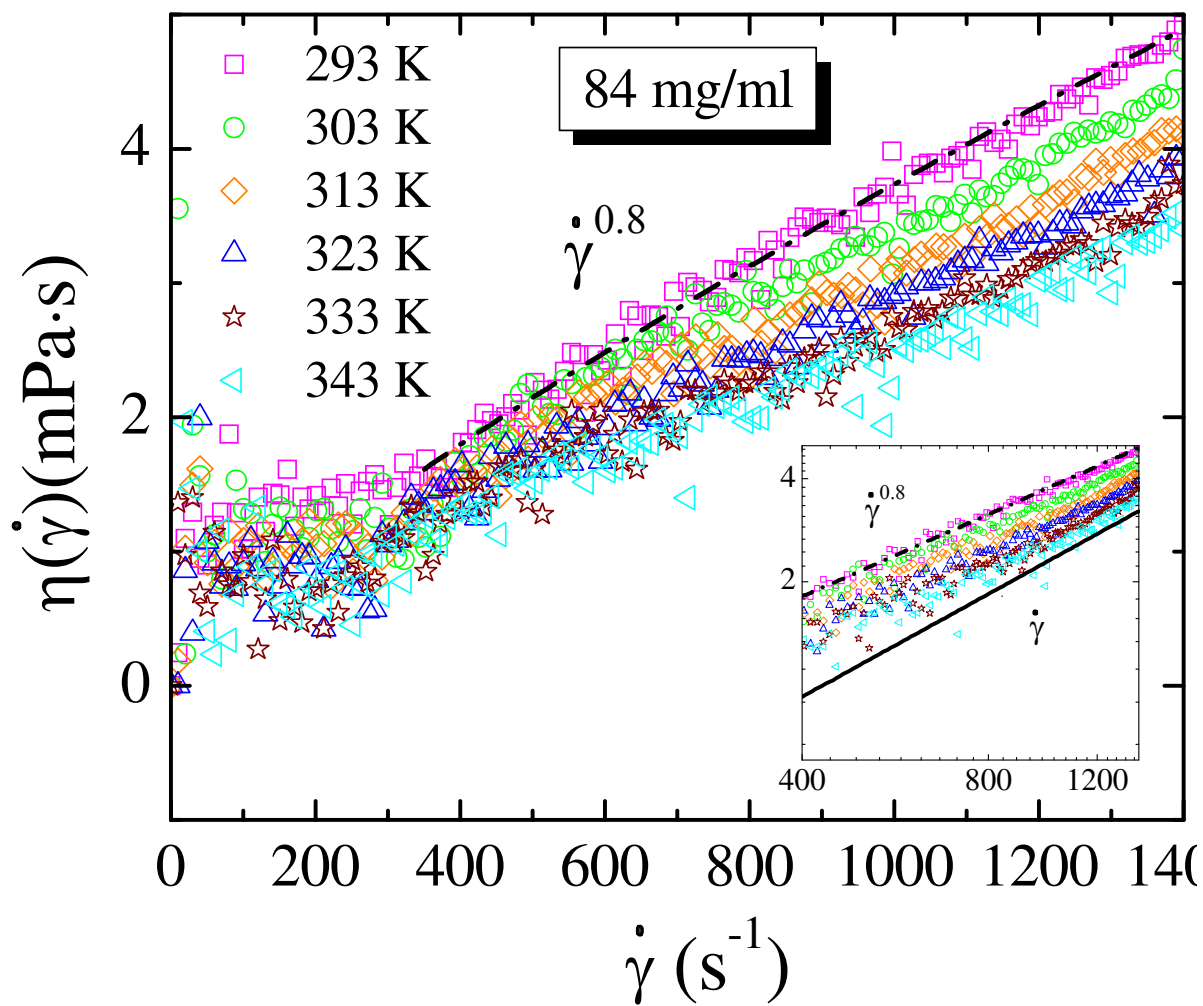


FIGURE 1

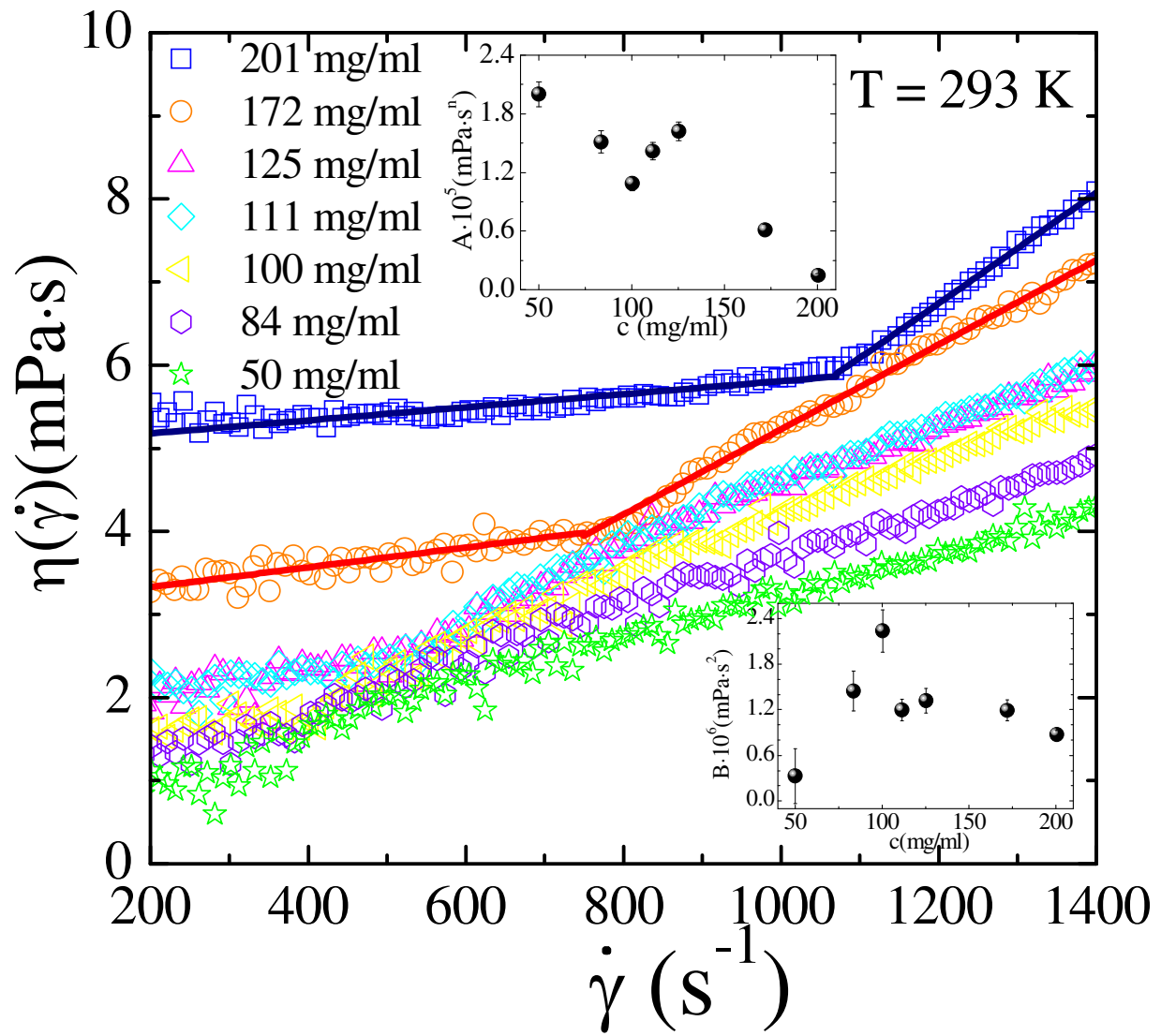


FIGURE 2

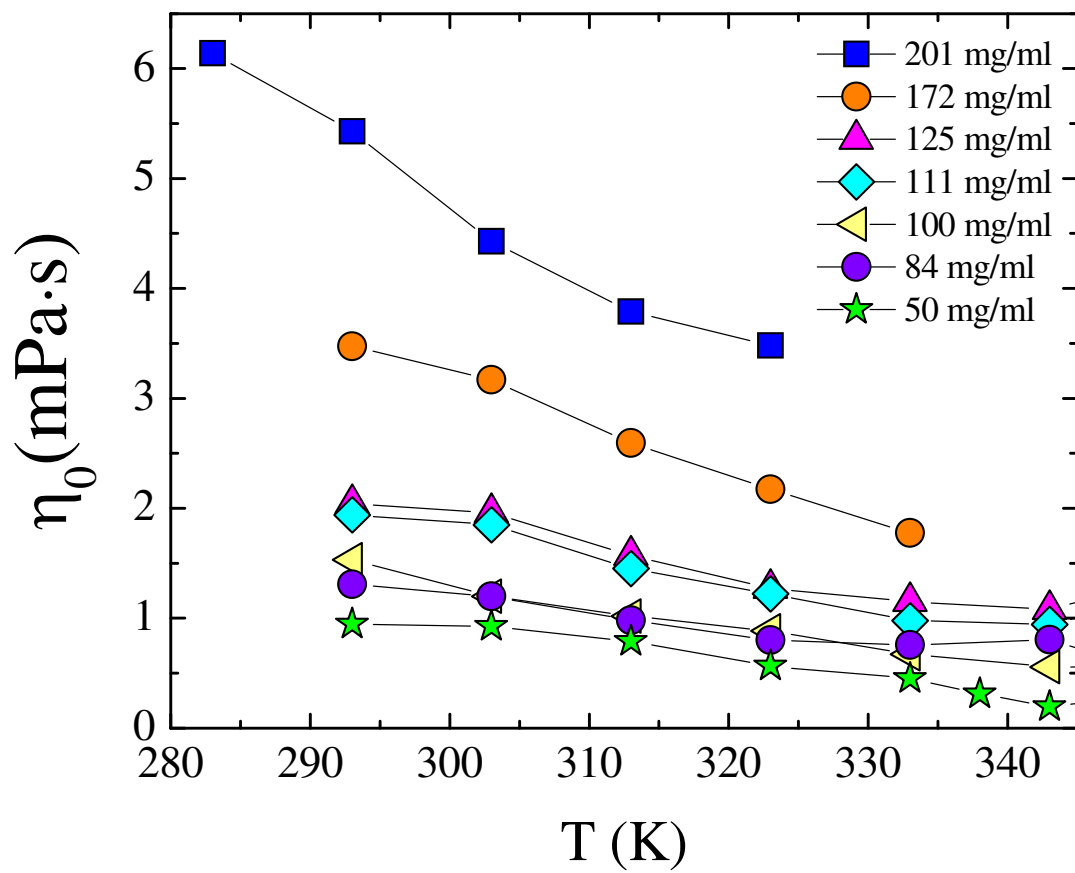


FIGURE 3

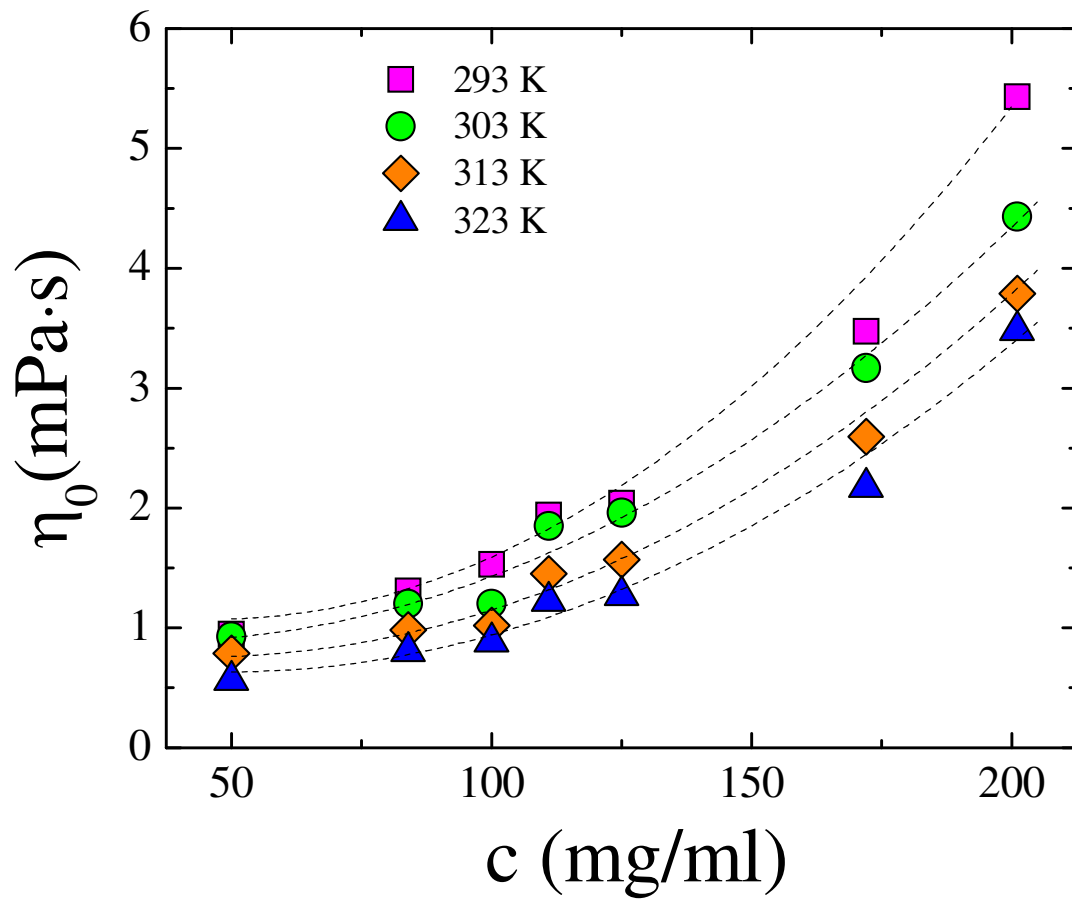
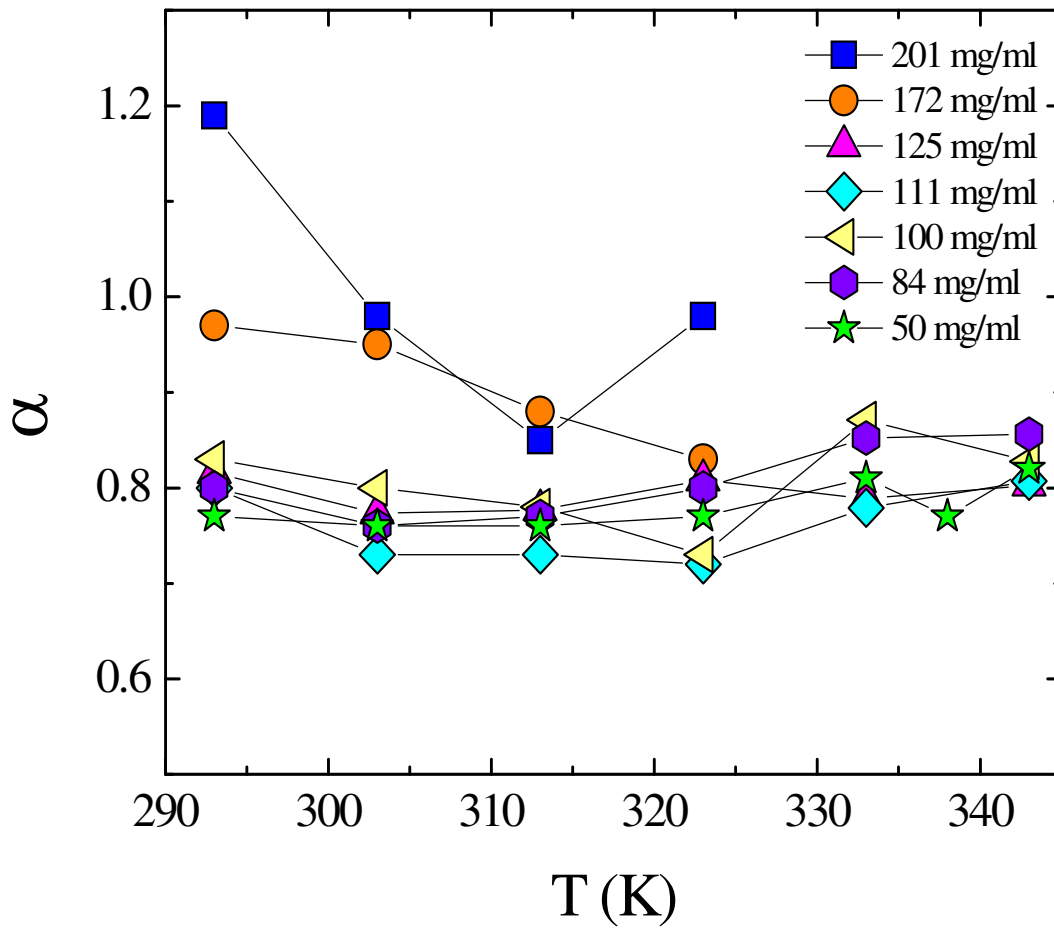


FIGURE 4



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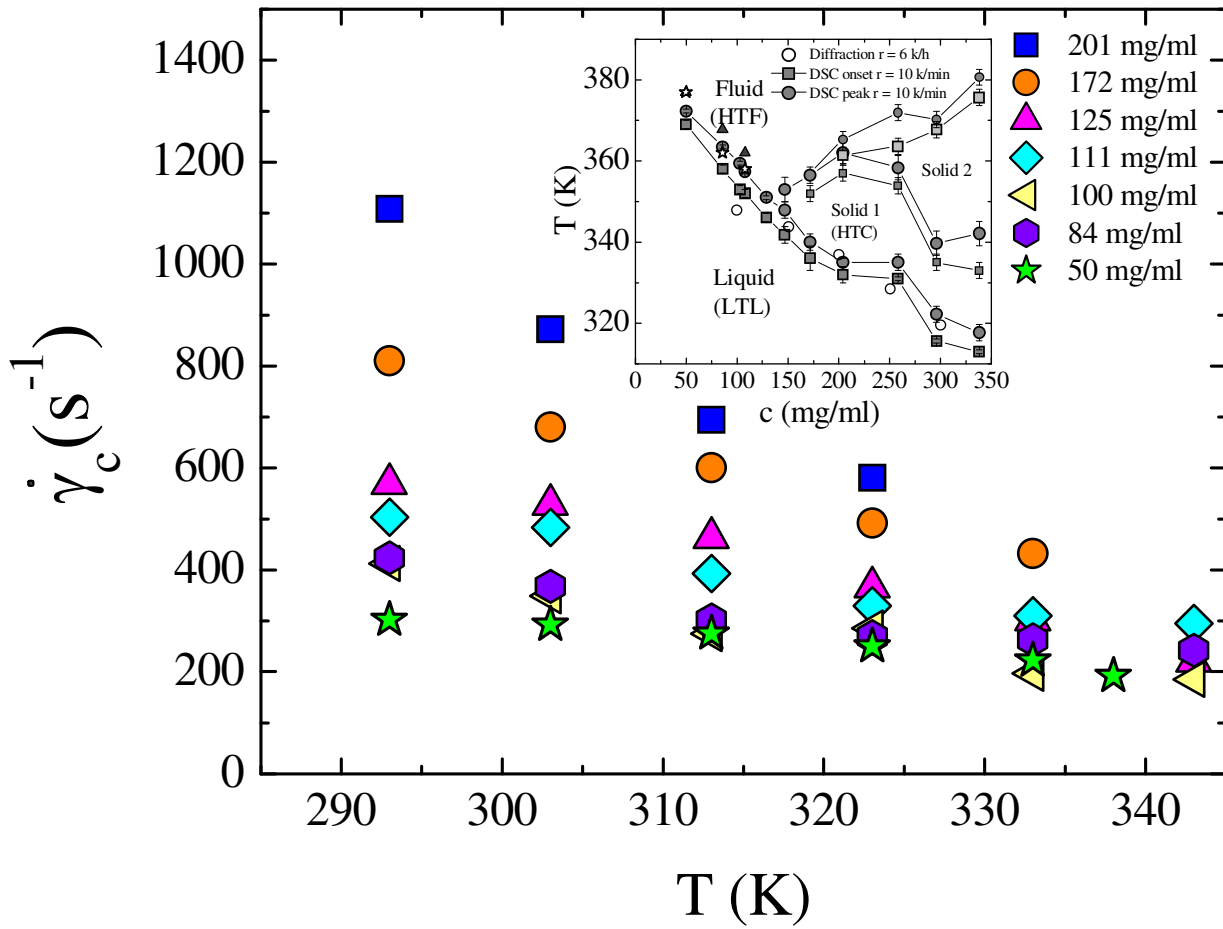


FIGURE 5