VISCOSITY OF HYDROXYPROPYL CELLULOSE SOLUTIONS
IN NON-ENTANGLED AND ENTANGLED STATES

MARIA BERCEA[*] and PATRICK NAVARD[**]

[*]*"Petru Poni" Institute of Macromolecular Chemistry, 41A, Ghica Voda Alley, 700487 Iași, Romania*
[**]*Mines Paristech, PSL – Research University, CEMEF – Centre de Mise en Forme des Matériaux, UMR CNRS 7635, CS 10207, Claude Daunesse Str., 06904, Sophia Antipolis Cedex, France*
✉*Corresponding authors: Maria Bercea, bercea@icmpp.ro;*
Patrick Navard, patrick.navard@mines-paristech.fr
Members of the European Polysaccharide Network of Excellence (EPNOE), www.epnoe.eu

Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 70th anniversary

The viscosity of isotropic hydroxypropyl cellulose (HPC) solutions was investigated in pure water and aqueous solution of 10% glucose as solvent. The intrinsic viscosity, $[\eta]$, was determined by using an approach developed by Wolf, which is able to describe the viscosity evolution over a large domain of concentrations (*c*) for any type of macromolecular structure. The transition between dilute solution (*i.e.* the state with isolated non-interacting coils) and semidilute solution (*i.e.* the state where coils are touching each other, but with not so many interactions between chains) was evidenced for the HPC solutions. Newtonian viscosity resulted from the flow curves determined in semidilute concentration regime. From the plot of the specific viscosity as a function of a dimensionless parameter, $c \times [\eta]$ (defined as reduced concentration), the entangled and non-entangled states were delimitated for the HPC aqueous solutions. A critical overlap parameter of 2.4 was determined. In aqueous solution of 10% glucose, the semidilute non-entangled state was depicted for high molecular HPC in the investigated range of concentrations (below 4 g/dL).

Keywords: hydroxypropyl cellulose, viscosity, non-entangled coils, entangled state

INTRODUCTION

Hydroxypropyl cellulose (HPC) is a biocompatible and water-soluble cellulose derivative used in many applications, including food, pharmaceutical and cosmetic products. It is widely used as a thickening or gelling agent and lubricant due to its rheological properties, as an emulsion stabilizer or for preparing capsules and films.[1-3]

HPC is soluble in cold water, but above 40 °C, a phase separation occurs with a decrease of viscosity and a sharp increase in turbidity.[4,5] It was shown that, below 39 °C, in dilute aqueous solution the HPC macromolecules exist in a single random coil state, showing a relatively broad distribution of the hydrodynamic radius. For higher temperatures (above 39 °C), water turns into a relatively poor solvent and hydrophobic interactions are exhibited. These conditions are favorable to the formation of aggregates and the gel spheres of high molecular weights.[6]

At room temperature, semidilute and concentrated aqueous HPC solutions, below a certain concentration, form an isotropic phase. Above this concentration, HPC is able to form an ordered liquid crystalline phase with a cholesteric structure.[5,7] This critical concentration depends slightly on molecular weight: it is located around 41% for $M_w = 8 \times 10^4$ g/mol, 42% for $M_w = 9.5 \times 10^4$ g/mol, and 39% for $M_w = 1.05 \times 10^6$ g/mol.[7]

The rheological behavior of HPC in liquid crystalline phase has been extensively investigated.[8-10] Due to the intrinsic orientation constraint, the liquid crystalline phase presents specific elastic behavior during deformation,[11] the magnitude of the stored energy being much higher as compared with those of isotropic polymer fluids. The polydomain morphology generates regions where local orthogonal orientations take place and provoke distortions upon cessation of

the flow and increase the elasticity during relaxation.[12]

In this paper, we focused on the viscous behavior of HPC in isotropic phase. Four HPC samples of different molecular weights were selected and their viscosities in pure water and aqueous solution of 10% glucose used as solvents were investigated. The main interest was to assess where the entangled and non-entangled states of HPC in solutions of different concentrations and molecular weights occur on the basis of their viscosity data.

EXPERIMENTAL

Klucel[TM] hydroxypropylcellulose (HPC) samples were kindly offered by Ashland Aqualon. For the present study, four samples were used: **E** – $M_w = 8\times10^4$ g/mol; **L** – $M_w = 9.5\times10^4$ g/mol; **G** – $M_w = 3.7\times10^5$ g/mol; **H** – $M_w = 1.05\times10^6$ g/mol (Table 1). Solutions of different concentrations were prepared by mixing the solvent and HPC at room temperature under magnetic action, stirring until a completely homogeneous solution was obtained. For the most concentrated systems, due to their high viscosity and elasticity, only mixing by hand was possible. In order to guarantee the attainment of thermodynamic equilibrium, the solutions were then agitated by means of a rolling mixer.

The following two solvents were selected: Millipore water and a solution of 10% glucose in water. Before analysis, the homogeneous solutions were left several days at rest at room temperature to remove air bubbles, in particular, for the most concentrated systems.

For the aqueous solutions of HPC, viscometric measurements were carried out at 25 °C, by using an Ubbelohde viscometer, capillary diameter type 0a of 0.53 mm (the flow time for water, t_o, was of 184.38 s). Rheological measurements were performed at 25 °C on a MCR 302 Anton Paar rheometer, equipped with a plate-plate geometry (diameter of the upper plate = 50 mm; gap = 500 μm) and a Peltier temperature control system.
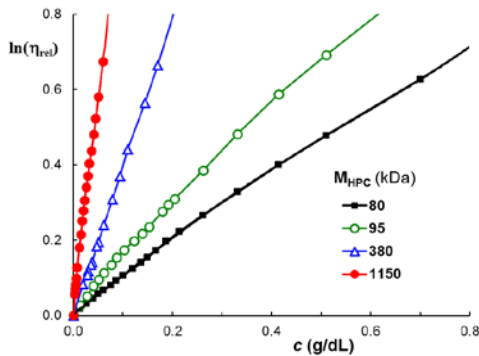
RESULTS AND DISCUSSION
Viscosity of dilute solutions

For Newtonian fluids, in the limit of infinite dilution, viscometric results can be analyzed by means of the following equation:[13]

$$\ln\eta_{rel} = \frac{c[\eta] + B c^2 [\eta][\eta]^\bullet}{1 + B c [\eta]} \qquad (1)$$

where η_{rel} is the relative viscosity ($\eta_{rel} = t/t_o$, the ratio between the flow time of the solution and of the solvent through the viscometer capillary); B represents the hydrodynamic interaction parameter, which is a system specific constant reflecting the polymer-solvent interaction, $[\eta]^\bullet$ is the specific characteristic hydrodynamic volume, a parameter used to model the observation that $\ln\eta_{rel}$ as a function of polymer concentration (c) becomes linear at sufficiently high concentrations.

According to Equation 1, $[\eta]$ can be determined from the initial slope of the dependence $\ln\eta_{rel}$ as a function of c at sufficiently low shear rates and polymer concentrations. Figure 1 shows these dependences for the aqueous solutions of four HPC samples with different molecular weights. The results of this evaluation are given in Table 1.

The intrinsic viscosity being correlated with the hydrodynamic volume occupied by a single chain, the critical overlapping concentration (which separates the dilute–semidilute regimes of concentration) can be calculated by using the Graessley model:[14]

$$c^* = 0.77/[\eta] \qquad (2)$$

with c^* scaling with the molecular weight as (Fig. 2):

$$c^* \sim M^{-0.88} \qquad (3)$$

Figure 1: Plot of $\ln\eta_{rel}$ as a function of c for aqueous solutions of HPC with different molecular weights
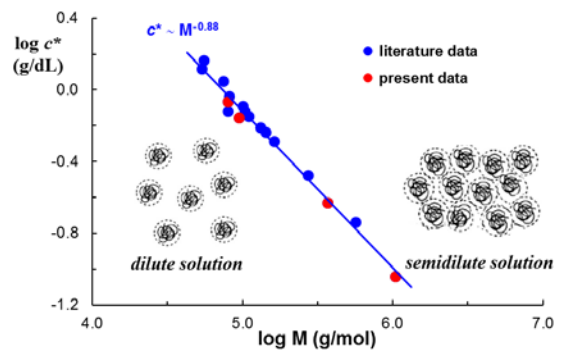

Figure 2: Delimitation of dilute – semi-dilute concentration regimes for HPC aqueous solutions

Table 1
Literature data[5,15] and present data for intrinsic viscosity of HPC in aqueous solutions[*]

Sample	M (kg/mol)	$[\eta]$ (dL/g)	c^* (g/dL)	Reference
	53.9	0.59	1.3051	Goodwin et al.[15]
	55.4	0.53	1.4528	Goodwin et al.[15]
	74.5	0.69	1.1159	Goodwin et al.[15]
	80	1.02	0.7549	Guido[5]
Klucel, E	80	0.90	0.8555	present data
	82.2	0.84	0.9167	Goodwin et al.[15]
Klucel, L	95	1.11	0.6960	present data
	101	0.95	0.8105	Goodwin et al.[15]
	103.8	1.02	0.7549	Goodwin et al.[15]
	110.0	1.09	0.7064	Goodwin et al.[15]
	131.7	1.25	0.6160	Goodwin et al.[15]
	142.5	1.33	0.5789	Goodwin et al.[15]
	163.6	1.49	0.5168	Goodwin et al.[15]
	273.8	2.31	0.3333	Goodwin et al.[15]
Klucel, G	370	3.29	0.2343	present data
	566.4	4.25	0.1811	Goodwin et al.[15]
Klucel, H	1150	8.49	0.0907	present data

[*]Critical overlap concentration, c^*, was calculated according to Equation 2

Viscosity of HPC in aqueous solutions

At constant temperature, the viscosity of HPC isotropic solutions depends on concentration, molecular weight of polymer and solvent, on the one hand, and on the shear conditions, on the other hand. During flow, a semidilute HPC solution of 0.1 g/dL behaves as a Newtonian fluid (Fig. 3), the viscosity (η) is independent of shear rate ($\dot{\gamma}$), covering the range of high $\dot{\gamma}$ (up to 1000 s^{-1}). By increasing the concentration above 0.3 g/dL, the Newtonian plateau is only present at low shear rates when the relaxation time of the deformed macromolecules is shorter than the characteristic time of the flow, keeping the overall structure of the solution in an isotropic state. At higher shear rates, the macromolecules have no time to fully relax and they tend to orient along the flow direction, leading to a non-Newtonian behavior with the viscosity depending on shear rate. The flow behavior can be observed either from viscosity or shear stress vs. shear rate.

For lower molecular weight HPC, the Newtonian plateau was observed for a larger range of concentrations (Fig. 4).

The non-Newtonian behavior appears around 20 g/dL with viscosity depending on shear rate only above 100 s^{-1}.

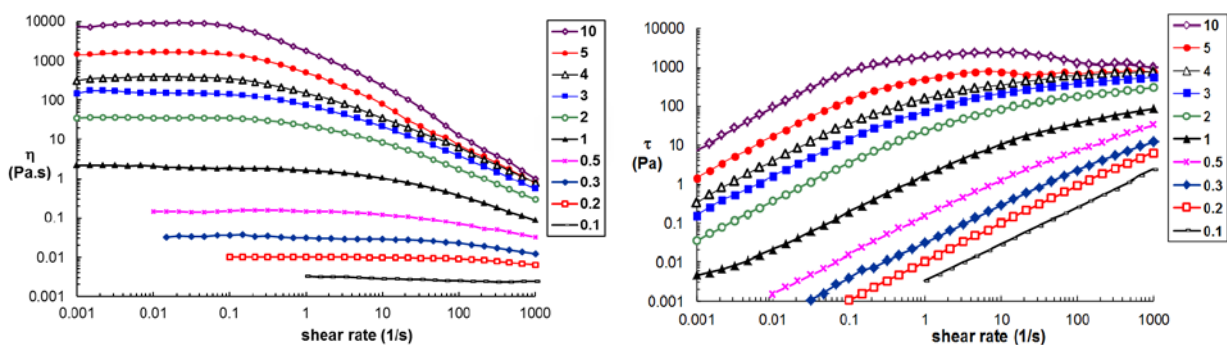As a first observation, the semidilute solutions behave as a Newtonian fluid.

Figure 3: Flow curves for HPC sample with M = 1.15×10^6 g/mol and different concentrations (g/dL) in water at 25 °C
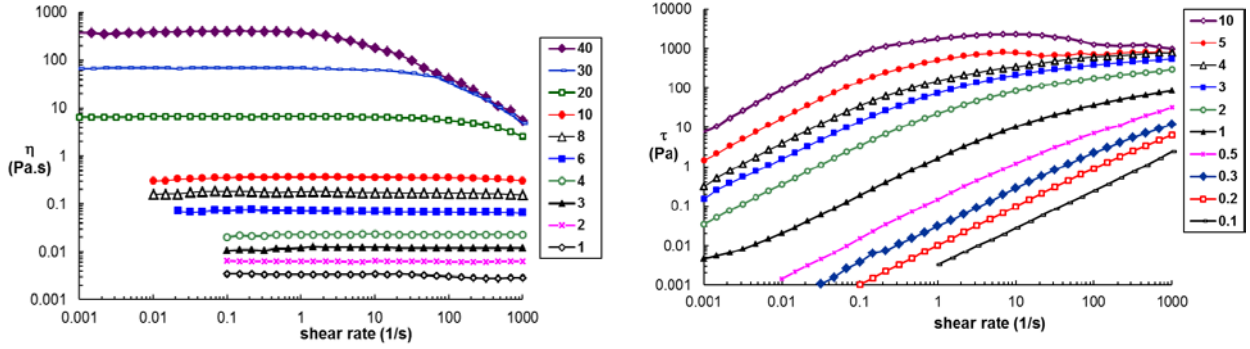
Figure 4: Flow curves for aqueous solutions of HPC with M = 8×10^4 g/mol and different concentrations (g/dL) in water at 25 °C
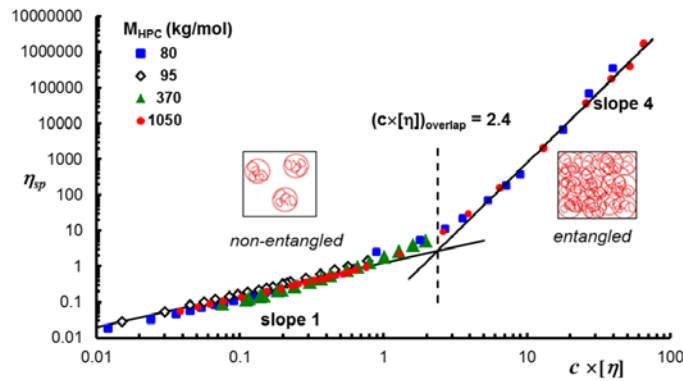

Figure 5: Specific viscosity as a function of $c \times [\eta]$ for HPC of different molecular weights and concentrations in aqueous solution at 25 °C

Now we try to distinguish the state of macromolecules in solution, if they are entangled or not. Figure 5 shows the dependence of the specific viscosity, η_{sp}, for HPC aqueous solutions at 25 °C as a function of the dimensionless reduced concentration, $c \times [\eta]$, which provides an indication of the total volume occupied by the polymer. This figure combines the data obtained from capillary viscometry with those obtained through rheological measurements. The experimental data describe two linear dependences delimited by the overlap reduced concentration $(c \times [\eta])_{overlap} = 2.4$. Below this limit, the HPC solutions behave as isolated chains during flow, η_{sp} varies linearly with $c \times [\eta]$. Above this value of overlap concentration (state attained by increasing either c or M), η_{sp} scales as $(c \times [\eta])^4$. In this region, the macromolecules both kinetically and hydrodynamically interact and they are in an entangled state. The chains form a temporary, reversible physical network, leading to a strong viscosity increase.

From the plot shown in Figure 5, we can estimate the state of the HPC solution (non-entangled or entangled) by determining the first Newtonian viscosity (under conditions of low shear rates) at a given concentration. The intrinsic viscosity can be calculated from the Mark-Houwink dependence reported for HPC in aqueous solutions at 25 °C:[15]

$$[\eta] = 3.47 \times 10^{-5} M^{0.88} \ (\text{dL/g}) \qquad (4)$$

Viscosity of HPC in glucose aqueous solutions

For high molecular weight HPC (M = 1.15×10^6 g/mol, Table 1), dissolved in 10% glucose aqueous solution, the intrinsic viscosity was determined by using the Wolf model with the relative viscosity obtained from the ratio of Newtonian viscosity at a given concentration and the viscosity of the solvent (Fig. 6). The solvent (solution of 10% glucose in water) has the viscosity of 1.9×10^{-3} Pa·s at 25 °C, about twice higher than that of water.

The flow curves for this system are given in Figure 6 and the plot of $\ln\eta_{rel}$ as a function of c used for the evaluation of $[\eta]$ is given in Figure 7.

Equation 1 was applied for polymers with different structures and architectures and the results have shown that it fits quite well the experimental data over a large range of concentrations, including the semidilute regime.[16-20] Thus, by modeling the dependences of $\ln\eta_{rel}$ as a function of c (shown in Fig. 7), the value of 13.99 dL/g for $[\eta]$ was obtained. This value is significantly higher than the value of 8.49 dL/g obtained for the intrinsic viscosity in pure water for the same HPC sample. The c^* value is 0.0715 g/dL for HPC in 10% glucose, meaning that all
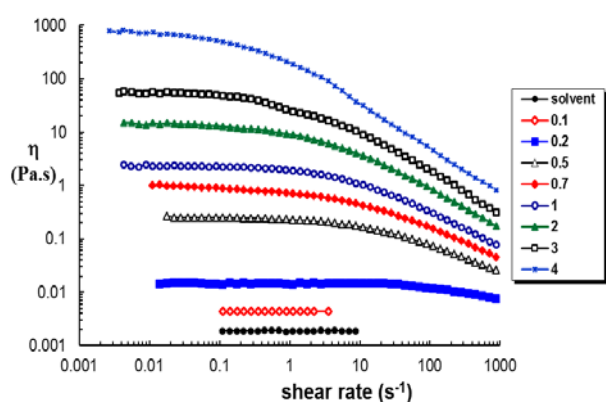
the rheological measurements were done in the semidilute non-entangled region of concentration.

These results suggest that the solvent quality is better in 10% glucose, compared to that in water, since the hydrodynamic volume of the HPC isolated coil is higher than those adopted in aqueous solutions (the long macromolecules having a more extended conformation and presenting high elasticity during deformation).[11] In addition, in the investigated range of concentrations, $\eta_{sp} \sim c \times [\eta]$, showing that the state with no hydrodynamic interactions between coils is depicted over a larger range of reduced concentration (as can be observed in Fig. 8).

Figure 6: Flow curves for HPC sample with M = 1.15×10^6 g/mol and different concentrations (g/dL) in 10% glucose aqueous solution at 25 °C
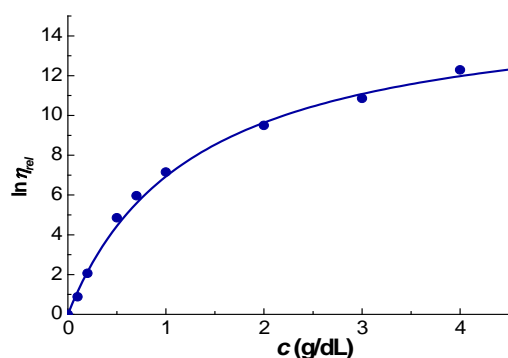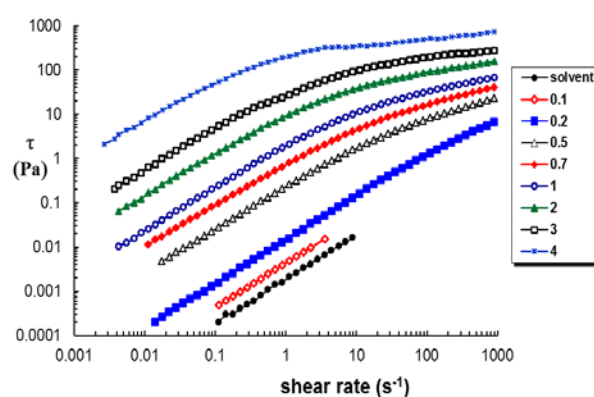

Figure 7: Plot of $\ln\eta_{rel}$ as a function of c for HPC sample with M = 1.05×10^6 g/mol in 10% glucose at 25 °C (the curve is obtained by fitting the experimental data with Equation 1)

Figure 8: Regions where the linear dependence $\eta_{sp} \sim c \times [\eta]$ was observed for HPC in different solvents at 25 °C

It can be observed that for $c \times [\eta]$ values well above 2.4, HPC is in a non-entangled state in the aqueous solution of 10% glucose. It can be appreciated that this solvent prevents the

formation of entanglements. In this study, the entangled state was below 4 g/dL in 10% glucose and the slope of η_{sp} vs. $c \times [\eta]$ dependence was close to unity. For higher concentrations, a plug

flow effect appears in the region of high shear rates.

CONCLUSION

By using the specific viscosity *vs.* $c \times [\eta]$ plots, we can get information concerning the macromolecular states of HPC chains. Thus, in aqueous solutions:

- $\eta_{sp} \sim c \times [\eta]$ (slope 1), $c \times [\eta] < 2.4$ – non-entangled (isolated) macromolecular coils;
- $\eta_{sp} \sim (c \times [\eta])^4$ (slope 4), $c \times [\eta] > 2.4$ – entangled macromolecules in a physical dynamic network.

The transition from the non-entangled state to the state where the macromolecular coils are isolated in an entangled network depends on the concentration and molecular weight, and it is influenced by the solvent. For 10% aqueous solution of glucose used as solvent, the region corresponding to the non-entangled state of HPC is more extended than in the case of water.

REFERENCES

[1] C. Clasen and W.-M. Kulicke, *Prog. Polym. Sci.*, **26**, 1839 (2001).
[2] D. Ishii, K. Ueda, P. Stroeve, T. Nakaoki and H. Hayashi, *Cellulose Chem. Technol.*, **50**, 755 (2016).
[3] L. Ochiuz, M. Hortolomei, I. Stoleriu and M. Bercea, *Cellulose Chem. Technol.*, **50**, 569 (2016).
[4] E. D. Klue, *J. Polym. Sci. Polym. Symp.*, **36**, 491 (1971).
[5] S. Guido, *Macromolecules*, **28**, 4530 (1995).
[6] J. Gao, G. Haidar, X. Lu and Z. Hu, *Macromolecules*, **34**, 2242 (2001).
[7] R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
[8] V. T. Tsakalos, P. Navard and E. Peuvrel Disdier, *Liq. Cryst.*, **21**, 663 (1996).
[9] M. D. Haw and P. Navard, *Rheol. Acta*, **39**, 280 (2000).
[10] V. V. Makarova, M. Y. Tolstykh, S. J. Picken, E. Mendes and V. G. Kulichikhin, *Macromolecules*, **46**, 1144 (2013).
[11] M. Bercea and P. Navard, *Cellulose Chem. Technol.*, **50**, 601 (2016).
[12] M. Bercea and P. Navard, *Macromolecules*, **33**, 6011 (2000).
[13] B. A. Wolf, *Macromol. Rapid Commun.*, **28** 164 (2007).
[14] W. W. Graessley, *Polymer*, **21**, 258 (1980).
[15] D. J. Goodwin, D. R. Picout, S. B. Ross-Murphy, S. J. Holland, L. G. Martini *et al.*, *Carbohyd. Polym.*, **83**, 843 (2011).
[16] B. A. Wolf, *Ind. Eng. Chem. Res.*, **54**, 4672 (2015).
[17] A. Spatareanu, M. Bercea, T. Budtova, V. Harabagiu, L. Sacarescu *et al.*, *Carbohyd. Polym.*, **111**, 63 (2014).
[18] M. Bercea, L. E. Nita, J. Eckelt and B. A. Wolf, *Macromol. Chem. Phys.*, **213**, 2504 (2012).
[19] C.-E. Brunchi, M. Bercea and S. Morariu, *J. Chem. Eng. Data*, **55**, 4399 (2010).
[20] X. Xiong, X. Huang and B. A. Wolf, *Food Hydrocoll.*, **72**, 195 (2017).