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EXPLORATORY RESEARCH PROJECT

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POLYMER MATERIALS WITH SMART PROPERTIES

- 2011 -

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BRIEF REPORT

concerning the investigations carried out by the project team

in the period October 5th, 2011 – December 15th, 2011

Objective:

Evaluation of intra- and inter-molecular interactions of natural and synthetic polymers in binary polymer/solvent systems

- Types of interactions occurring in solutions of natural and synthetic polymers

- Peculiar behaviors of natural or synthetic polymers in solution and how to model them

Introduction

Water-soluble polymers present special physicochemical properties that recommend them for use in many areas of industry, environment, medicine, agriculture, etc. The use of polymer materials in various area depends on their ability adsorption/interaction with different particle substrates, ions, solubilization of low molecular weight compounds (hydrocarbons, dyes, drugs), modification of the rheological properties of aqueous systems in a specific way. The interaction between water-soluble polymers and solid particles can influence the stability of colloidal suspensions. Polymer selection is dictated both by the intrinsic characteristics of macromolecules (nature of the functional groups, molecular weight, chemical structure), dispersion properties (concentration and particle size, ionic strength) and the characteristics of the environment (pH, temperature). The destabilization of water-soluble polymers in suspension is an important effect in the phase separation processes such as solid-liquid separation (coagulation, flocculation, etc.). Synthetic polymers present better performances than natural ones, but may contain traces of toxic monomers and additives. Natural polymers are non-toxic and biodegradable and suitable for such applications.

In this stage, some preliminary investigations were carried out for systems which will be deeply studied during the next years.

Experimental Part

Materials: **Natural polymers: Chitosan** (CS, Aldrich); **Xanthan** (Aldrich);

 Synthetic polymers: Pluronic F127 (PL, BASF); **Poly(aspartic acid)** (PAS, synthetized by Dr. A. Chiriac)

Methods: **Capillary viscometer** Lauda;

 Stress control **rheometer** Bohlin CVO (Malvern);

 Zetasizer Nano-ZS (Malvern Instruments);

 HACH 2100AN **turbidimeter**.

Results and Discussion

The **chitosan** is a polysaccharide with several unique properties such as biodegradability, biocompatibility, non-toxicity, antibacterial activity and it is an excellent candidate for biomedical applications, cosmetics and food industry. We investigated the viscometric behavior of chitosan in aqueous solutions in the presence of acetic acid (AcOH) at 25 ° C. Fedors equation [*Polymer*, 20, 225, (1979)] allows a smooth linearization of experimental data (Figure 1):

$$\frac{1}{2\left(\eta_r^{1/2}-1\right)} = \frac{1}{c[\eta]} - \frac{1}{c_m[\eta]} \tag{1}$$

η_r - relative viscosity; c_m - a parameter correlated with the packing degree of macromolecular chains; $[\eta]$ - intrinsic viscosity, c - concentration of polymer.

Recently, a new approach was presented in literature [Wolf et al., *Macromolecules*, 41, 912 (2008); *Macromol. Rapid Commun.,* 28, 164 (2007)] which allows the determination of the intrinsic viscosity for polymer solutions by knowing the viscometric behaviour at low polymer concentrations and shear rates:

$$\ln \eta_r = \frac{c[\eta]_W + Bc^2[\eta]_W[\eta]^\bullet}{1 + Bc[\eta]_W} \tag{2}$$

B – hydrodynamic interaction parameter; $[\eta]^\bullet$ - characteristic specific hydrodynamic volume.

The equation (2) has been successfully used to study both neutral polymer and polyelectrolyte solutions. Table 1 present comparative data obtained by Fedors and Wolf methods for chitosan solutions in solvents with different ionic strengths.

Table 1. Viscometric data obtained by applying the Fedors and Wolf methods for chitosan in water/AcOH solutions

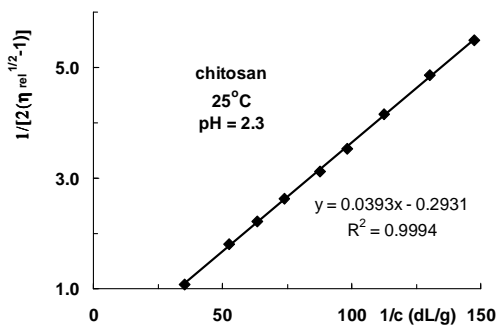| Solvent	pH	$[\eta]_F$ dL/g	c_m	$[\eta]_W$ dL/g	B
1.75 M AcOH	2.3	25.445	0.1347	25.403	0.100
0.60 M AcOH	2.6	31.645	0.1226	30.499	0.102
0.44 M AcOH	2.7	37.594	0.0998	37.658	0.201
0.35 M AcOH	2.8	39.683	0.0524	40.630	0.062
0.03 M AcOH	3.4	59.524	0.0435	57.623	0.027

Figure 1. Dependence type Fedors (equation (1)) for chitosan solutions at pH 2.3.
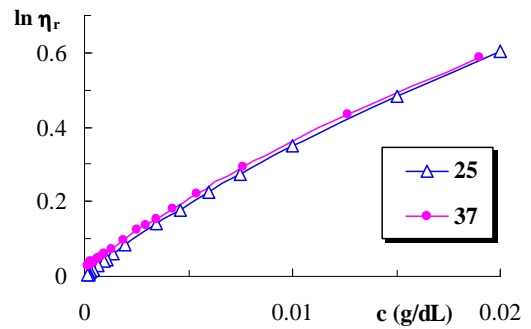

Figure 2. Wolf dependence (equation (2)) for xanthan solutions in water at 25°C and 37°C.

We also explored the viscometric behaviour of **xanthan** solutions in water at 25°C (room temperature) and 37°C (near the body temperature). The application of Huggins and Fedors methods to determine the intrinsic viscosity at 25°C and 37°C was not possible due to the fact that the dependences are not linear, making difficult the interpretation of the experimental data. This problem can be avoided if the experimental data are modeled with the new approach of Wolf.

In Figure 3, the dependence of kinematic viscosity on reciprocal absolute temperature for different concentrations of xanthan aqueous solutions is shown. From the plots, the flow activation energy was determined as being around 15 KJ/(mol°K) [R = 8,314 J/(mol.K)].
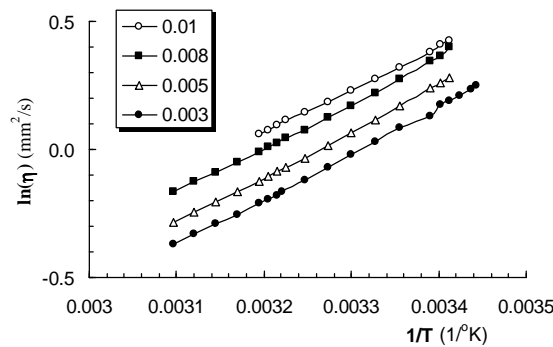

Figure 3. η = f(1/T) for aqueous solutions of xanthan(different concentrations indicated on the plot). T is the absolute temperature.

Poly(aspartic acid) (PAS) is an ideal component for biodegradable systems and it is ogf high interest for designing materials for biomedical applications. Due to presence of its carboxyl group in the structure of polymer chains, PAS acts as a weak polyelectrolyte in aqueous medium at neutral pH. In aqueous media, each of the carboxyl group of repeating PAS unit structure will lose proton and becomes negative, PAS becoming stronger sensitive to slight variations in pH of the medium. At pH = 6.5 or higher (basic solutions), it dissociates completely, showing high electrical charge in solution.
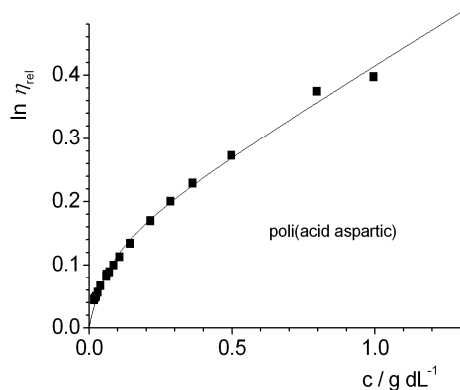
Figure 4. Modeling the concentration dependence of the natural logarithm of relative viscosity according to Wolf (equation (2)) for the aqueous solutions of PAS at 25°C.
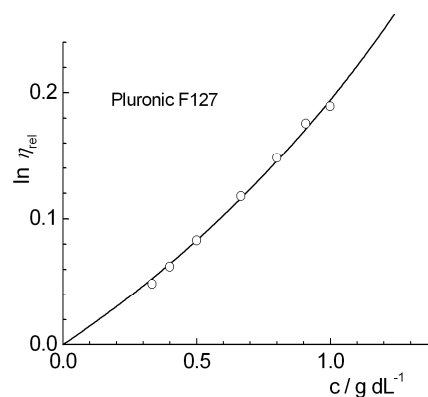

Figure 5. Modeling the concentration dependence of the natural logarithm of relative viscosity according to Wolf (equation (2)) for the aqueous solutions of Pluronic F127 at 25°C.

Pluronic F127 (PL), is a macromolecular surfactant with the chemical formula PEO_{99}–b–PPO_{69}–b–PEO_{99}, where PEO is poly(ethylene oxide) and PPO is poly(propylene oxide). PL in aqueous solutions, at high enough concentration, forms close-packed medium consisting of spherical micelles (18 nm in diameter) in aqueous solution. The nanoscale micelles completely fill space with a locally ordered lattice. The difference in the water affinity of PEO and PPO depends on temperature. At low temperatures, both subunits are generally hydrophilic and soluble in water. At room temperature, however, PPO subunits become preferentially hydrophobic and more insoluble than PEO subunits. As the temperature increases, the PPO block's hydrophobicity increases, so that PPO subunits attract each other but repel water, being screened from water by the PEO subunits. PPO blocks overlap, surrounded by the hydrophilic ends in order to form micelles at room temperature (higher than 17°C) [see as for example: *J. Phys. Chem. B* 114 (2010) 4171; *Coll. Surf. B* 103 (2013) 544, *Polym. Plast. Technol. Eng.,* 53 (2014) 1354]. Figures 4 and 5 show the Wolf dependence for PAS and PL aqueous solutions. The two PAS and PL samples present close molecular weights (1.5×10^3 g/mol and 1.27×10^3 g/mol), but their intrinsic viscosities differ considerably. Table 2 presents several characteristics of these polymers determined in aqueous solutions at 25°C.

Table 2. Hydrodynamic diameter, intrinsic viscosity, zeta potential and conductivity for PAS an PL aqueous solutions at 25°C

Sample	Hydrodynamic diameter (nm)	[η] (mL/g)	Zeta Potential (mV)	Conductivity (mS/cm)
PAS	280	245.3	-23	0.2
PL	10	20.5	-7.8	3.5

In 2011 (in less than 3 months), the project team has started a few exploratory investigations for some polymers which are of high interest for the next investigations having the main objective the design of *stimuli-responsive polymers.* **The proposed objective for 2011 was realized.**

Dissemination of the results: A manuscript was elaborated in 2011, finalized and published in 2012: Morariu S., Brunchi C.-E., Bercea M., The behaviour of chitosan in solvents with different ionic strengths, *Industrial & Engineering Chemistry Research*, **51(39),** 12959-12966 (2012)