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Viscosity–temperature–concentration relationship for starch–DMSO–water solutions

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Abstract

The rheological behavior of starch–DMSO–water solutions was monitored using a cone-plate rheometer at different temperatures and concentrations. A solvent ratio DMSO/water = 80/20 was used and viscosity was correlated with temperature through the Arrhenius equation. The dilute to semidilute flow regime transition concentration, c^* (which was independent of temperature), was characterized by a change in the value of apparent energy of activation. At $c < c^*$, it was shown that the pre-exponential term in the Arrhenius equation was a function of concentration. Deviations from the predicted dependence was also used to characterize change in the flow regime. The value of c^*, obtained from the apparent energy of interaction and the pre-exponential term agreed with the one obtained from the usual plot of log η_{sp} vs. log c. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Viscosity–temperature dependence; Arrhenius equation

1. Introduction

There are many theories dealing with the viscosity–temperature relationship in liquids and polymers, which use the concept of free volume (Haward, 1970), and equations derived from this concept have been used in the description of the behavior of polymer solutions (Haseebuddin, Raju, Krishna, & Yaseen, 1996). In this work, the correlation between viscosity and temperature for starch–DMSO–water solutions at different concentrations is analyzed in terms of some of these concepts. The Arrhenius equation (Eq. (1)), which has already been employed to describe the temperature dependence of dilute polymer solutions (Gupta & Yaseen, 1997) is used to describe our system

$$\eta = \eta_0 e^{\frac{E_A}{RT}}, \tag{1}$$

where η_0 is a pre-exponential constant and E_A is the apparent energy of activation. The above authors used this equation to analyze solvency power of solvents and solvent blends. In the present work, we emphasize the use of both E_A and η_0 as indicators of a change in the flow regime for starch–DMSO–water systems.

2. Experimental

2.1. Preparation of solutions

A given solution was prepared by heating potato starch (Reagen, A.C.S. grade, weighed on a dry basis), water and DMSO (Reagen, P.A.) 80/20 (DMSO/water) under effective stirring at 80°C for 30 min. Stirring was continued for 24 h., at room temperature, before the analysis was carried out. For each concentration, viscosity was monitored at 25°C for 5 days. A constant value indicated that complete solubilization was achieved. All solutions were filtered, using a glass porous filter (#G4), prior to experiments in the rheometer.

2.2. Measurement of viscosity

Viscosity measurements were carried out in a cone-plate type Brookfield rheometer, model DV-III, using spindle CP41. All the measurements were performed within a torque range from 10 to 90% of its full scale.

The experimental error involved in the torque measurement was 1% of its full scale, regardless of the measured torque.

2.3. Calculation of parameters

The parameters E_A and ln η_0, as well as their associated errors (ΔE_A and Δln η_0, respectively) were calculated from

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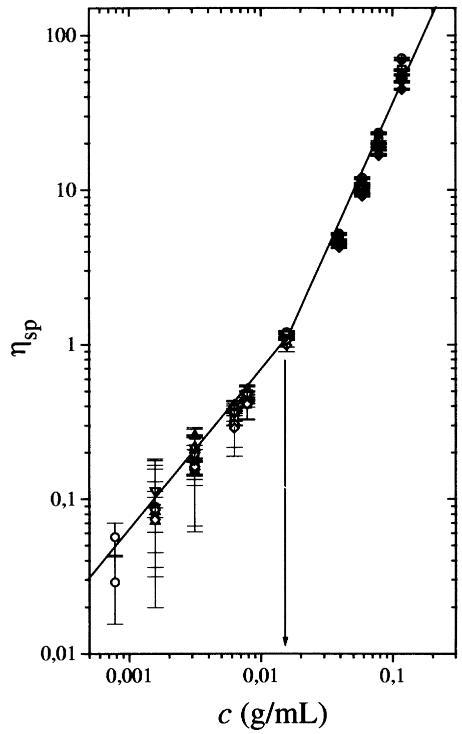

Fig. 1. The specific viscosity vs. concentration plot for starch–DMSO–water solutions: (○) 5°C; (△) 25°C; (▽) 35°C; and (◇) 45°C.

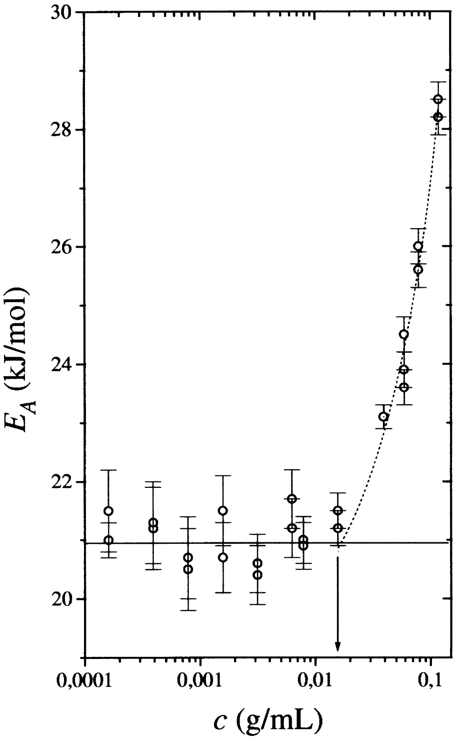

Fig. 2. An apparent energy of activation vs. concentration for starch–DMSO–water solutions.

the linearization of Eq. (1) as

$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT}, \tag{2}$$

through the minimization of the χ square merit function (Press, Teukolsky, & Vetterling, 1993)

$$\chi^2 = \sum_{i=1}^{N} \left(\frac{\ln \eta_i - \ln \eta_0 - (E_A/RT)}{\Delta \ln \eta_i} \right)^2, \tag{3}$$

where $\Delta \ln \eta_i$ is the experimental error associated with $\ln \eta_i$, being given by the following expression (Taylor, 1993) and $\Delta\eta_i$ is the experimental error in the measurement of the viscosity η_i obtained from the uncertainty in the viscometer torque.

$$\Delta \ln \eta_i \cong \left| \frac{d \ln \eta_i}{d\eta_i} \right| \Delta\eta_i = \frac{\Delta\eta_i}{\eta_i}. \tag{4}$$

3. Results and discussion

The solutions showed a Newtonian behavior within the range of shear rate used in this work. Fig. 1 shows the dependence of specific viscosity on the concentration for starch–DMSO–water solutions, at different temperatures. There is a master curve, which encompasses all the temperatures used in this work, although data fit is poorer for lower concentrations. Fig. 1 also shows that, regarding concentration dependence, there are two regions, which can be characterized by the two different slopes in the double-logarithmic plot. They have already been characterized in literature as a consequence of two kinds of behavior: one in which the individual polymer molecules are present as isolated coils, which is related to the line with a lower slope; another one in which the total hydrodynamic volume of individual chains exceeds the volume of the solution (Morris, Cutler, Ross-Murphy, Rees, & Price, 1981). As a consequence, there is significant coil overlap and inter-penetration, which results in stronger polymer–polymer interactions and higher viscosity.

More specifically, it reinforces already established theories which claim that random coil polymers obey a universal behavior expressed through the existence of a unique $\log \eta_{sp}$ vs. $\log c[\eta]$ master curve (where η_{sp} and $[\eta]$ are the specific and intrinsic viscosities, respectively). Deviations from this master curve are attributed to specific molecular interactions creating “hyper-entanglements” (Morris et al., 1981; Launay, Cuvelier, & Martinez-Reyes, 1997). Since the analysis carried out in this work was of phenomenological character, it is not possible to assert what kind of specific interaction we have, apart from that (for higher concentrations) its occurrence is a function of temperature, as we will subsequently show in this work, by an analysis of the apparent flow energy of activation. Launay et al., 1997 have suggested that there are two critical concentrations, c^*, the point from which there is an initial departure from linearly ($c^*[\eta] \approx 0.80$) and c^{**} ($c^{**}[\eta] \approx 6$) which delimit three regimes: dilute ($c < c^*$), semidilute

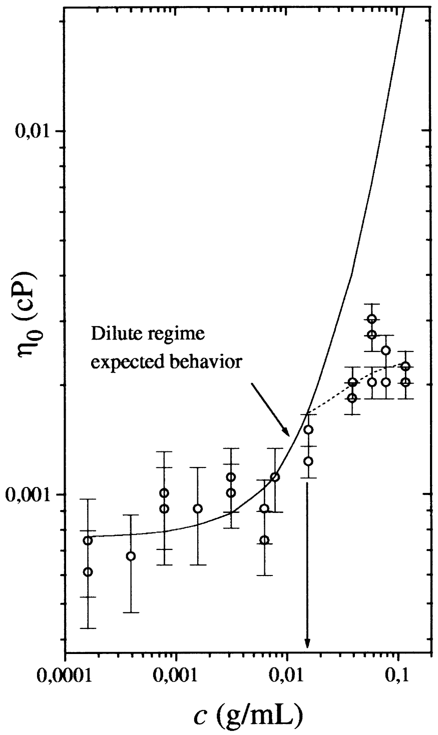

Fig. 3. η_0 vs. concentration for starch–DMSO–water solutions. The continuous curve is obtained from Eq. (7).

($c^* < c < c^{**}$), and concentrated ($c > c^*$). It can be seen that there is a discontinuity in the curve at $c \approx 0.015$ g/ml, which, in a master curve would correspond to a value of $c[\eta] \approx 0.8$; this concentration would correspond, therefore, to the transition from the dilute to the semidilute regime. The highest concentration used in this work corresponded to a value of $c[\eta] = 6.3 \pm 0.3$; that would explain the absence of c^{**} in this plot. Since, in the present case, intrinsic viscosity was not necessary to build the master curve, it follows that, for this system, $[\eta]$ is independent of temperature. Its value was calculated according to Mark–Huggins equation (Eq. (5)) (Flory, 1953) as 50 ± 2 ml/g.

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta] + k'[\eta]^2 c. \tag{5}$$

Values of intrinsic viscosity for starch, amylopectin and amylose in different solvent conditions can be found in literature (Cowie, 1961; Salemis & Rinaudo, 1984), and a value in the same range has been found for an amylose sample ($[\eta] \approx 60$ ml/g and DMSO/water solvent composition = 66/34) (Cheetham and Tao, 1981).

Eq. (1), adequately described the viscosity–temperature dependence for all the concentrations analyzed in this work. It is, therefore, reasonable to plot the apparent energy of activation (E_{A}) against concentration. Fig. 2 shows that the value of E_{A} is constant below $c \approx 0.015$ g/dl, continuously rising, afterwards. A constant value of E_{A} reflects the fact that, in the dilute regime, viscosity is solely a function of polymer–solvent and solvent–solvent interactions. At concentrations above c^*, E_{A} is expected to change, due to occurrence of polymer entanglement: a new type of interaction starts playing its role and as concentration is increased, polymer–polymer interactions become more significant and, as a result, there is a continuous increase in E_{A}.

A more quantitative approach can be carried out if one takes Mark–Huggins equation as the starting point. Rearranging Eq. (5) in terms of solution viscosity, $\eta(c)$, and solvent viscosity, $\eta(0)$, it follows that

$$\eta(c) = [1 + [\eta]c + k'([\eta]c)^2]\eta(0). \tag{6}$$

The superposition of the points in Fig. 1 showed that neither $[\eta]$ nor k', significantly varies with temperature. Consequently, $\eta(c, T)$ can be expressed, when in the dilute solution regime, according to Eq. (1), where

$$\eta_0 = \eta_0(c) = [1 + [\eta]c + k'([\eta]c)^2]\eta_0(0); \quad E_{\mathrm{A}} = E_{\mathrm{A}}(0). \tag{7}$$

Here, $E_{\mathrm{A}}(0)$ and $\eta_0(0)$, respectively are the values of the apparent activation energy and pre-exponential constant for the pure solvent, a change in the value of E_{A} indicating a change in the flow regime.

Finally, values obtained for η_0 are plotted against concentration in Fig. 3 as well as the graphical representation of Eq. (7) for this system. The curve was built using the experimentally obtained values of $[\eta]$, $k'[\eta]^2$ (the slope of the η_{sp}/c vs. c plot) and $\eta(0)$. It can be seen that η_0 ceases to be a function of c, as described by Eq. (7), at approximately the same concentration, indicating a change in the flow regime, which is consistent with what has been found from the η_{sp} vs. c and E_{A} vs. c data.

4. Conclusion

The temperature dependence of starch–DMSO–water solutions (DMSO/water = 80/20) can be adequately described using the classical Arrhenius expression. The apparent energy of activation, as well as the pre-exponential term can be used as a way of characterizing a change in the flow regime. This is particularly apparent as an abrupt change in the value of apparent energy of activation.

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