Use of Intrinsic Viscosity for Evaluation of Polymer-Solvent Affinity

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ABSTRACT

The objective of the current paper was to define a rheological method for the study of the solvent/binder affinity. The adopted strategy involves the study of the intrinsic viscosity [η] of polymer solutions. [η] was estimated via an extrapolation procedure using the Huggins and Kramer equations.

The effects of chemical structure and molecular weight on the polymer/solvent affinity were investigated. Rheological properties of Ethyl Cellulose (EC), Polyvinyl Butyral (PVB) and Polyvinyl Acetal (PVAc) resins in a solution of a high boiling point glycol ether solvent were explored and compared. The intrinsic viscosity and the Mark-Houwink shape parameter were estimated for the three polymers and used as criteria for estimating the polymer/solvent affinity.

INTRODUCTION

Ethyl Cellulose (EC) polymer is extensively used in different formulations [1]. The most commonly used EC has a degree of ethyl ether substitution of about 2.4-2.5. This degree of substitution confers useful properties such as water resistance with excellent solubility properties both in polar and non-polar organic solvent [2]. These features make the polymer a multifunctional material which can be used as film former, thickener for perfumes and body creams (waterproof sunscreens), rheology modifier and binder in ceramic applications [1].

Promising alternative polymers have received attention for their application as film former, binder, plasticizer and thickener. Among them extremely attractive for their water resistant and organic solubility properties are Polyvinyl Butyral (PVB) and Polyvinyl Acetal (PVAc) [3-5].

Most the applications mentioned requires a suspension/solution (colloidal) processing approach. A key issue in the formulation of a polymer solution is the affinity between polymer and solvent. It is directly related to the intrinsic viscosity, [η] [6,7]. The [η], for a solute in a given solvent, is defined as the solute ability of isolated polymer molecule to increase the solvent viscosity [6]. The methods for the determination of [η] can be divided into those involving extrapolation of experimental data at a series of dilute concentrations (extrapolation method) [6, 7], and those involving estimation of [η] from a single viscosity measurement on a dilute solution (single point method) [6, 7]. The extrapolation method offers a precise procedure for determination of [η], whereas the single point method is quicker and can be valuable for routine analysis of a large amount of samples.

In the current work the extrapolation method was used to evaluate the compatibility between the mentioned

polymers and a high boiling point glycol ether solvent.

The effect of chemical structure and molecular weight in determining the compatibility were investigated. The intrinsic viscosity and Mark-Houwink shape parameter were estimated and used as criteria for evaluating polymer/solvent compatibility.

EXPERIMENTAL
Materials

Ethyl Cellulose materials, with a degree of substitution of 2.4-2.5 (48-49 % of ethoxyl content), were purchased from Dow Chemical Corporate. Ethyl cellulose of four different molecular weights were investigated, ranging from 76 kDa to 212 kDa (see Table 1).

Polyvinyl Butyral (PVB) and Polyvinyl Acetal (PVAc) of different molecular weights (see Table 1) were purchased from Sekisui. The chemical compositions of the PVAc and PVB resins used are reported in Table 2.

Glass transition temperatures obtained by the suppliers are reported in Table 1.

All the polymeric materials were used as received.

A high boiling point Glycol Ether (Mw >300 g·mol^{-1}, density ~ 1 g·cm^{-3}) was used as solvent. It was used as received.

Samples preparation

The polymer solutions were prepared by a dilution method. The appropriate amount of a concentrated solution, typically 1 g·dl^{-1}, was taken with a micro pipette and added to a volumetric flask. Then, the required volume of solvent was added. The solutions were then gently rolled at 21°C overnight prior to measurements.

PVB and PVA samples are referred to by the supplier grade code (*e.g.* BL-S, BH-S). Ethyl cellulose samples are referred to using the capitol letters EC followed by the number for the corresponding Ethocel™ material, *e.g.*10. The Ethocel™ number identifies the viscosity of a 5% solution of the polymer in toluene/ethanol 80:20 at 25 ºC.

Rheological characterization

The rheological properties of suspensions were measured with a rotational rheometer (RheoStress 600, controlled stress/rate rheometer, Haake) using a cone plate configuration with an angle of 1 degree and a diameter of 60 mm. A constant temperature of 21°C was maintained during the experiments using a DC30 temperature control unit.

Flow Curve Tests (FCT) were performed in a stepped mode using 45 steps with a waiting time of 2s. The investigated ranges of shear rates were from 0.1 s^{-1} up to 100 s^{-1}, in the upwards ramp, and from 100 s^{-1} to 0.1 s^{-1} in the downwards ramp.

In a typical measurement procedure, 5-6 concentrations were prepared and measured for each polymer. Data is expressed as the means of at least three replications with the corresponding standard deviations.

RESULTS AND DISCUSSION

Ethyl Cellulose (EC) is one of the most commonly used polymers in many formulations. Consequently its properties in solution have been studied extensively. In Figure 1 (a), (b), and (c), the chemical structure for the three kinds of polymers investigated in this work are shown. The two other materials investigated, PVB and PVAc, possess similar molecular structure (Figure 1b and c) but have a different main substituent, Butyral and Acetal group, respectively, yielding a slightly different polarity and flexibility of the two polymers.

One of the most significant features of adding polymer to a solution is the intense increment in the viscosity that it produces. The intrinsic viscosity [η] corresponds to the ability of an isolated polymer molecule to increase the viscosity of the solvent in the absence of intermolecular interactions between polymer molecules. The intrinsic

viscosity is related to the spatial extension of the polymer in solution and therefore also depends on the goodness of the solvent.

Table 1. Polymers Molecular weight and Glass transition temperature.

Polymer	Grade	Mw (kDa)	Glass Transition Temperature (°C)
Polyvinyl Butyral (PVB)	BL-S	23	61
	BM-S	53	60
	BH-S	66	64
Polyvinyl Acetal (PVAc)	KS-10	17	106
	KS-1	27	107
	KS-3	108	110
	KS-5	130	110
Ethyl Cellulose (EC)	EC-10	76.7	119
	EC-20	120	125
	EC-45	155	121
	EC-100	212	129

Table 2. Chemical composition for PVB and PVA resins.

Polymer	Grade	Acetal Cont. (%mol)	Butyral Cont. (%mol)	Hydroxyl Cont. (%mol)
Polyvinyl Butyral (PVB)	BL-S	/	74±3	~22
	BM-S	/	73±3	~22
	BH-S	/	73±3	~22
Polyvinyl Acetal (PVAc)	KS-10	74±3	/	~25
	KS-1	74±3	/	~25
	KS-3	74±3	/	~25
	KS-5	74±3	/	~25

Therefore, the study of intrinsic viscosity has been proposed as an effective method to assess polymer/solvent affinity and the conformation of the polymer in solution [7]. In a good solvent, polymer coils tend to repel one another. The polymer units prefer to be solvated and thus possess a rather extended molecular conformation. When neither polymer self-interactions nor polymer-solvent interactions dominate the theta condition is satisfied. At the theta point the polymer is unperturbed and displays minimal expansion. On the other hand, in a poor solvent, attractive forces among polymer chain units prevail and the polymer chains tend to contract.
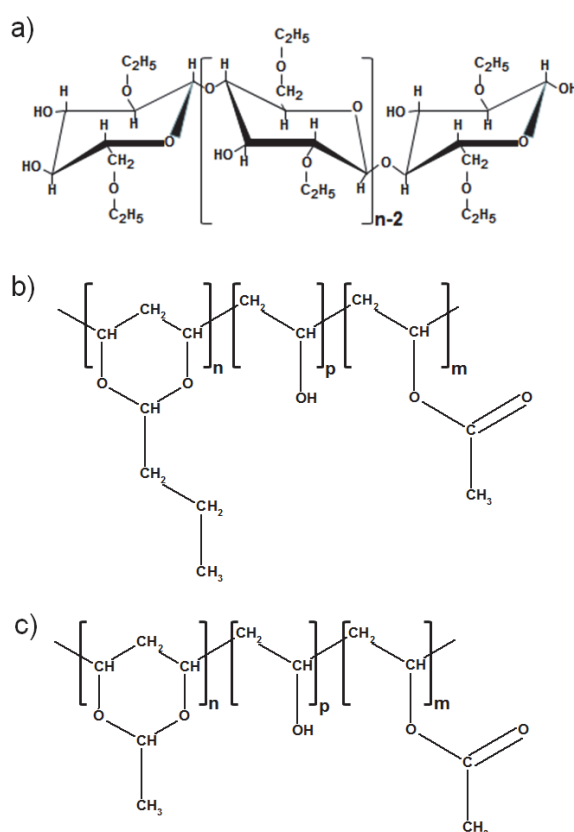

Figure 1. Chemical structure for a) Ethyl Cellulose, b) Polyvinyl Butyral (PVB), and c) Polyvinyl Acetal (PVA).

The intrinsic viscosity can be determined either by the extrapolation method or by single point determination. In both cases experiments are performed on dilute solutions. Dilute solution ensures an ideal situation for which the individual polymer coils are well separated from one another, and interactions among polymer coil are

negligible [6, 7]. Therefore, this situation enables to evaluate the contribution of each single coil to the rheological properties of the whole solution.

Several semi-empirical relations have been proposed for both methods [7].

In this work the extrapolation procedure was adopted and the most commonly used equations for determining [η], Huggins (1) and Kramer (2), were used:

$$\eta_{sp}/c=[\eta]+K_H[\eta]^2c \qquad (1)$$

$$(\ln \eta_r)/c=[\eta]-K_K[\eta]^2c \qquad (2)$$

where η_r is the relative viscosity, η_{sp} is the specific viscosity (η_r -1), η_{sp}/c is the reduced viscosity, $(\ln \eta_r)/c$ is the inherent viscosity, and K_H, and K_K are Huggins, and Kramer constants, respectively. The Intrinsic Viscosity [η] is obtained by extrapolation of the reduced viscosity (η_{sp}/C) or inherent viscosity ($\ln(\eta_r/c)$) to zero concentration. The extrapolation method requires a linear dependence of the reduced or inherent viscosity as function of concentration. Therefore, limitations on the concentration range must be defined in order to satisfy the linearity requirement. The Huggins and Kramer equation have been found to be strictly applicable for [η]c<<1. For concentrations higher than those indicated, the influence among the single polymer coil is not any longer negligible and it affects the flow properties leading to a deviation from the linear trend.

Huggins and Kramer coefficients are considered adequate criteria to evaluate the quality of the solvent [6, 7]. Experimental results indicate that the higher the affinity between polymer and solvent, the lower is the K_H value. A range varying from 0.25 to 0.5 is attributed to good solvatation, whereas values above 0.5-1.0 are found for poor solvents. At the theta point, Huggins constant is 0.5. The closer its value is to 0.3, the higher is the affinity between polymer

and solvent [7]. At the same time, negative values for the Kramer constant indicate good solvents and positive values indicate poor ones [6, 7].

Table 3. Huggins viscosities ([η]) and constants.

Polymer	Grade	[η]$_H$ (dl/g)	K$_H$ (g/dl)
Polyvinyl Butyral (PVB)	BL-S	0.56±0.02	0.41±0.07
	BM-S	0.96±0.02	0.44±0.06
	BH-S	1.23±0.05	0.41±0.07
Polyvinyl Acetal (PVAc)	KS-10	0.51±0.05	0.32±0.07
	KS-1	0.80±0.02	0.31±0.07
	KS-3	1.76±0.08	0.29±0.09
	KS-5	2.03±0.06	0.40±0.06
Ethyl Cellulose (EC)	EC-10	0.92±0.03	0.32±0.06
	EC-20	1.22±0.04	0.42±0.07
	EC-45	1.70±0.09	0.44±0.09
	EC-100	2.29±0.10	0.25±0.06

Table 4. Kramer viscosities ([η]) and constants.

Polymer	Grade	[η]$_K$ (dl/g)	K$_K$ (g/dl)
Polyvinyl Butyral (PVB)	BL-S	0.57±0.01	-0.10±0.04
	BM-S	0.97±0.01	-0.10±0.03
	BH-S	1.24±0.03	-0.08±0.04
Polyvinyl Acetal (PVAc)	KS-10	0.52±0.03	-0.18±0.03
	KS-1	0.80±0.02	-0.17±0.05
	KS-3	1.74±0.05	-0.17±0.05
	KS-5	2.03±0.03	-0.13±0.03
Ethyl Cellulose (EC)	EC-10	0.91±0.02	-0.15±0.04
	EC-20	1.23±0.02	-0.12±0.04
	EC-45	1.72±0.05	-0.12±0.05
	EC-100	2.32±0.06	-0.21±0.04

In Figures 2, 3, and 4 the Huggins and Kramer plots are shown for PVB, PVAc, and EC polymers, respectively. The [η] values obtained by the extrapolation together with the corresponding constants

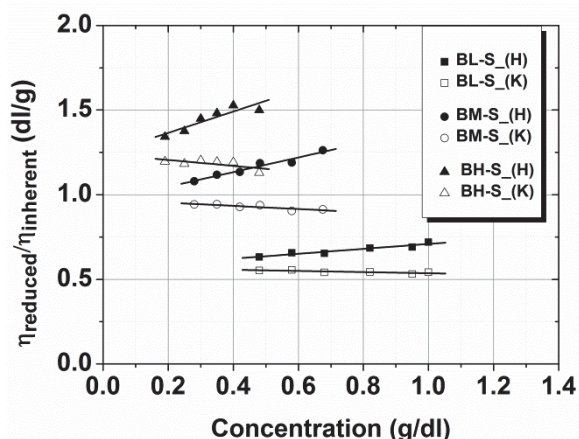are tabulated in Table 3, and 4 for Huggins and Kramer relations respectively.

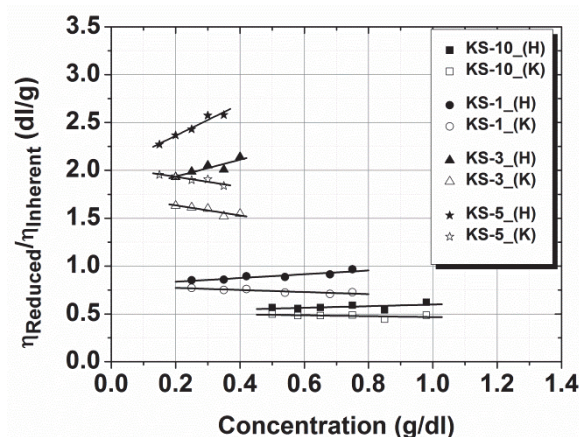Figure 2. Huggins (H) and Kramer (K) plots for PVB.

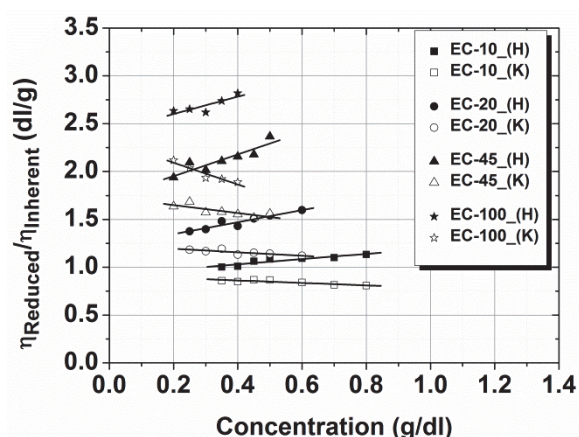Figure 3. Huggins (H) and Kramer (K) plots for PVAc.

Figure 4. Huggins (H) and Kramer (K) plots for EC.

The three equations provide values for the intrinsic viscoisty which are, within the experimental error, in good agreement with one another. According to this analysis, the solvent used is a good solvent for the selected polymers. In fact, as indicated in the Tables, all the K_H values vary in the range of good solvent, with values lower than 0.5. This conclusion is further supported by the negative values for the Kramer constants (K_K).

Specifically, the analysis of the Huggins and Kramer coefficients indicates that the polymers with the greatest affinity for the Glycol Ether used in this work are the materials KS-10, KS-1, and EC-10 displaying K_H values close to 0.30. This indicates that molecule presents a flexible and extended conformation and the polymer-solvent interactions are stronger than polymer self-interactions (intra- and inter-molecular interactions).

The conformation of the polymer in solution can be further investigated using the semi-empirical Mark-Houwink equation, which relates the intrinsic viscosity and the molecular weight[8, 9]:

$$[\eta]=KM_w^a \qquad (3)$$

where K and a are empirical constants specific to the polymer-solvent pair at specified temperature. They are a measure of the "stiffness" of the chain. Specifically, the a constant is called shape parameter and it is directly related to the polymer conformation in a solution of a given solvent. It is equal to 0 in a very poor solvent in which the polymer precipitates. Its value ranges from 0 to 0.5 in a poor solvent, in which the polymer exhibits a compact conformation. Its value is equal to 0.5 at the *theta* point. In a good solvent, polymer chains prefer to interact with solvent thus exhibiting a flexible extended conformation and the shape parameter varies from 0.5 to 0.8. Values in the range of 0.8-1.0 are characteristic for semi-flexible

macromolecules such as cellulose derivatives [8]. It varies in the range from 1.0 to 1.8 for highly extended chains, such as polyelectrolyte in solution of very low ionic strength [8].
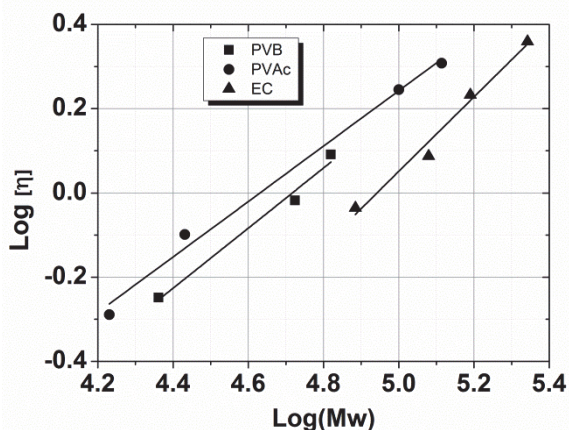

Figure 5. Mark-Houwink plot for PVB, PVAc, and EC.

In its logarithmic form Mark-Houwink equation enables a quick estimation of the involved parameters by simple linear regression. In Figure 5 the double logarithmic Mark-Houwink plot for the polymers investigated is shown.

Results for the shape parameter, a, are reported in **Table 5**. The values estimated experimentally for the three kinds of chemical structures vary in the range of 0.61-0.88, thus confirming significant affinity between the selected solvent and the investigated polymers. As a consequence of its less flexible structure, EC exhibits the highest value (0.88 ± 0.08) indicating an extended conformation in solution. This result is in agreement with what is reported in literature for such inherently semi-flexible macromolecules[8]. The shape parameter for PVB and PVAc resins are (0.71±0.09) and (0.66±0.04), respectively, which are typical values for a random coil conformation. It is worth observing that PVB resins exhibit a higher value of the shape parameter than the resins belonging to PVAc type. The obtained Kramers and Huggins coeffients

indicate that the solvent is better for PVAc than for PVB, but PVB still displays a marginally higher Mark-Houwink shape parameter for PVB, corresponding to a larger spatial extension of PVB in the studied solvent. We ascribe this to the greater excluded volume of PVB as compared to that of PVAc, caused by the longer pendant (butyral) substituent groups on PVB than on PVAc (acetal). This effect influences also the intrinsic viscosities. In fact, as indicated in Figure 5, PVB resins possess lower [η] values. This is in agreement with what is expected based on the observed differences in the spatial conformation (or compactness) as estimated from the Mark-Houwink shape factors. More compact conformation is expected to yield a greater resistance to flow, hence the higher viscosity.

Consequently, EC materials exhibit the lowest intrinsic viscosities out of the studied polymers. The analysis of the Mark Houwink shape parameter correlates well with the obtained Huggins and Kramer coefficients.

Table 5. Mark-Houwink shape parameter (α).

Polymer	Grade	a
Polyvinyl Butyral (**PVB**)	BL-S	
	BM-S	0.71±0.09
	BH-S	
Polyvinyl Acetal (**PVAc**)	KS-10	
	KS-1	0.66±0.04
	KS-3	
	KS-5	
Ethyl Cellulose (**EC**)	EC-10	
	EC-20	0.88±0.08
	EC-45	
	EC-100	

CONCLUSION

In this study polymer/solvent affinity was estimated via an intrinsic viscosity method. An extrapolation procedure was

adopted based on linear regression using the Huggins and Kramer equations. Intrinsic viscosity and the Mark-Houwink shape parameter for Ethyl Cellulose (EC), Polyvinyl Butyral (PVB) and Polyvinyl Acetal (PVAc) resins dissolved in a glycol ether solvent were estimated and compared.

The analysis of the critical coefficients, Huggins and Kramer constants, together with the study of the Mark-Houwink shape parameter enable to establish that the selected Glycol Ether is a good solvent for all polymers investigated in this study. The PVAc and PVB resins exhibit quite similar behaviour, whereas EC is significantly more extended in solution, due to the semi-flexible nature of cellulose.

ACKNOWLEDGMENTS

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