

# VISCOMETRIC STUDIES OF CHITOSAN/POLYACRYLAMIDE MIXTURES

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## **Abstract**

*Polymer-polymer interactions and miscibility for chitosan (Ch) and partially hydrolysed polyacrylamide (HPAM) have been investigated using dilute solution viscosity. The intrinsic viscosity,  $[\eta]$ , and the viscosity interaction parameters,  $b_m$ , have been determined for the binary (solvent/polymer) and ternary (solvent/polymer A/polymer B) systems. Degree of miscibility of these polymer mixtures was estimated on the basis of two criteria. The final result depends on (i) the applied extrapolation method used for determination of the interaction parameters, (ii) the assumed miscibility criteria, and (iii) the blend composition.*

**Key words:** *chitosan, polyacrylamide, polymer blends, miscibility criteria, viscosity interaction parameters.*

## **1. Introduction**

The principal derivative of chitin is chitosan (Ch) - poly[ $\beta$ -(1 $\rightarrow$ 4)-2-amino-2-deoxy-D-glucopyranose] [1, 2]. Chitosan can be considered a good candidate for the preparation of new biopolymer mixtures owing to its potentially attractive properties. Chitosan has been used in diverse areas such as medicine, pharmacy, and the food and cosmetic industries. The partially hydrolysed polyacrylamide (HPAM) is a copolymer of acrylamide and sodium acrylate [3] and is a water-soluble synthetic anionic polyelectrolyte. Polymer/polymer blending is an important and well-established method to improve the original properties of one or both components. In this paper, mixtures composed of chitosan with partially hydrolysed polyacrylamide at different component ratios have been prepared as material designed for different applications e.g. in medicine or pharmacy.

Several techniques, such as differential scanning calorimetry, FTIR analysis, DMA and high-resolution solid state  $^{13}\text{C}$  NMR spectroscopy, have been used to investigate the polymer-polymer interactions and miscibility in polymer mixtures. However, viscometric analysis is a simple, quick and an inexpensive method to study polymer-polymer interactions in solution [4 - 10].

The purpose of this study was to evaluate the miscibility of two chitosans, with different molecular weights, using partially hydrolysed polyacrylamide on the basis of experimental and ideal values of the viscosity interaction parameters, which were calculated from viscosity measurements in dilute Ch/HPAM solution mixtures.

## **2. Materials and methods**

### **2.1 Materials**

Partially hydrolysed polyacrylamide is a commercial polymer from Sigma Aldrich with a degree of hydrolysis (DH) of 1.5% and a viscosity average molecular weight of  $1.5 \times 10^6$ . The degree of deacetylation of both chitosans was 78% and the viscosity average molecular weights were  $0.5 \times 10^6$  for Ch I and  $1.4 \times 10^6$  for Ch II. Both chitosan samples were supplied by Sigma Aldrich.

Ch and HPAM samples were solubilised separately in aqueous 0.1M  $\text{CH}_3\text{COOH}/0.2\text{M}$  NaCl. Ternary solutions for each system were prepared by mixing the appropriate quantity of polymer solutions in the weight ratios  $w_A:w_B$  of 0.2:0.8, 0.5:0.5 etc.

### **2.2 Methods**

Viscosity measurements of dilute polymer solution ( $c = 0.1\%$ ) were carried out in an Ubbelohde capillary viscometer. The flow times were recorded with an accuracy of  $\pm 0.01$  s, and the bath temperature was constant ( $25 \pm 0.1$  °C). Before measurements, the solutions were filtered through G1 sintered glass filters. The intrinsic viscosity and the Huggins coefficient values were determined according to the Huggins equation [11, 12], using 5 solution concentrations. Kinetic energy corrections were taken into account for the evaluation of the intrinsic viscosity, which was determined by extrapolation to infinite dilution (zero solute concentration).

The miscibility was estimated by comparison of the experimental and ideal values of  $b_m^{\text{exp}}$  and  $[\eta]_m^{\text{exp}}$ . The values of  $b_m^{\text{exp}}$  and  $[\eta]_m^{\text{exp}}$  were determined from the plot of  $\eta_{\text{sp}}/c$  vs  $c$  (**Equation 1**) for solutions containing both polymers.

$$\frac{(\eta_{\text{sp}})_m}{c_m} = [\eta]_m + b_m c_m \quad (1)$$

where:  $b_m^{\text{exp}}$  = the experimental viscosity interaction parameter of the polymer mixture;  $[\eta]_m^{\text{exp}}$  = the experimental, intrinsic viscosity of the polymer blends;  $[\eta]_m$  = intrinsic viscosity of the polymer blends; and  $c_m$  = total concentration of solution.

Krigbaum and Wall [4] have defined the ideal value of the interaction parameter  $b_m^{\text{id}}$  by the expression:

$$b_m^{\text{id}} = b_A w_A^2 + b_B w_B^2 + 2b_{AB}^{\text{id}} w_A w_B \quad (2)$$

$$b_{AB}^{\text{id}} = b_A^{1/2} b_B^{1/2} \quad (3)$$

where:  $b_A$ ,  $b_B$ ,  $b_{AB}$  = interaction parameters of like (AA, BB) and unlike (AB) polymer molecules, respectively; and  $w_A$ ,  $w_B$  = weight fractions of polymers A and B, respectively.

The polymer blend is miscible if  $\Delta b_m = b_m^{\text{exp}} - b_m^{\text{id}} > 0$  and immiscible if  $\Delta b_m = b_m^{\text{exp}} - b_m^{\text{id}} < 0$ .

Garcia et al. [5] defined the ideal value of the interaction parameter,  $b_m^{\text{id}}$ , as:

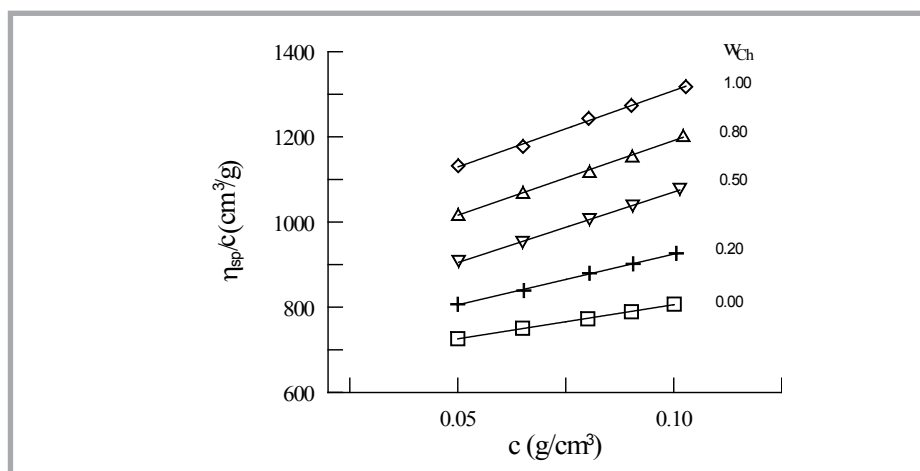
$$b_m^{\text{id}} = b_A w_A^2 + b_B w_B^2 \quad (4)$$

Additionally, Garcia et al. [5] proposed another miscibility criterion based on the difference between the experimental and ideal values of  $[\eta]_m$ . If  $\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}} < 0$  the system is miscible, and if  $\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{id}} > 0$  the system is immiscible. The value of  $[\eta]_m^{\text{exp}}$  was determined from the intercept of the plot according to **Equation 1**, whereas  $[\eta]_m^{\text{id}}$  was obtained from **Equation 5**.

$$[\eta]_m^{\text{id}} = [\eta]_A w_A + [\eta]_B w_B \quad (5)$$

### 3. Results and discussion

The plots of reduced viscosity ( $\eta_{\text{sp}}/c$ ) versus concentration ( $c$ ) for Ch II and HPAM and their mixtures in different weight fractions of chitosan are shown in **Figure 1**. The linear relationships are observed for the polymers and all of mixtures over whole composition range. The plots of  $\eta_{\text{sp}}/c$  versus  $c$  for Ch I/HPAM (not shown here) and the Ch II/HPAM mixtures lies between the plots for the virgin polymers. Therefore, interactions between polymeric components are not very strong [4, 6, 10].



**Figure 1.** The reduced viscosity versus polymer concentration for Ch II, HPAM and their mixtures in  $0.1 \text{ mol}\cdot\text{dm}^{-3} \text{CH}_3\text{COOH} + 0.2 \text{ mol}\cdot\text{dm}^{-3} \text{NaCl}$  at  $25^\circ\text{C}$ ;  $w_{\text{Ch}}$  is the weight fraction of chitosan.

The parameters of the miscibility criteria proposed by Krigbaum et al. [4] and by Garcia et al. [5] were calculated using **Equations 1 - 5** and are tabulated in **Tables 1 - 2**. It can be observed for Ch I/HPAM mixture solutions that the parameter  $\Delta b_m$  values are positive, with the exception of the composition of the low content of Ch in the mixture ( $w_{\text{Ch}} = 0.2$ ),

**Table 1.** A comparison of the dependence of the experimental and ideal viscometric parameters of the Ch I/HPAM blends on the assumed definitions of the ideal values of these parameters. Solvent:  $0.1 \text{ mol}/\text{dm}^3 \text{CH}_3\text{COOH}/0.2 \text{ mol}/\text{dm}^3 \text{NaCl}$ ;  $w_{\text{Ch}}$  = the weight fraction of chitosan.  $b_m^{\text{id*}}$  - determined according to Krigbaum and Wall [4],  $b_m^{\text{id**}}$  - determined according to Garcia et al. [5].

$w_{\text{Ch}}$	$b_m^{\text{exp}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$b_m^{\text{id*}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$\Delta b_m$	$b_m^{\text{id**}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$\Delta b_m$	$[\eta]_m^{\text{id}}$ [ $\text{cm}^3/\text{g}$ ]	$[\eta]_m^{\text{exp}}$ [ $\text{cm}^3/\text{g}$ ]	$\Delta[\eta]_m$
0.8	0.684	0.602	8190	0.337	34,670	456.3	431.6	-24.68
0.5	0.956	0.921	3480	0.508	44,850	527.2	473.2	-54.00
0.2	1.301	1.308	-700	1.043	25,800	598.1	538.3	-59.82

**Table 2.** A comparison of the dependence of the experimental and ideal viscometric parameters of the Ch II/HPAM blends on the assumed definitions of the ideal values of these parameters. Solvent:  $0.1 \text{ mol}/\text{dm}^3 \text{CH}_3\text{COOH}/0.2 \text{ mol}/\text{dm}^3 \text{NaCl}$ ;  $w_{\text{Ch}}$  = the weight fraction of chitosan..  $b_m^{\text{id*}}$  - determined according to Krigbaum and Wall [4],  $b_m^{\text{id**}}$  - determined according to Garcia et al. [5].

$w_{\text{Ch}}$	$b_m^{\text{exp}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$b_m^{\text{id*}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$\Delta b_m$	$b_m^{\text{id**}} \times 10^5$ [ $\text{cm}^3/\text{g}$ ] <sup>2</sup>	$\Delta b_m$	$[\eta]_m^{\text{id}}$ [ $\text{cm}^3/\text{g}$ ]	$[\eta]_m^{\text{exp}}$ [ $\text{cm}^3/\text{g}$ ]	$\Delta[\eta]_m$
0.8	3.509	3.129	38,000	2.362	114,700	888.8	840.3	-48.54
0.5	3.315	2.498	81,700	1.299	201,600	797.6	783.9	-58.65
0.2	2.383	1.937	44,600	1.170	121,300	706.3	686.2	-20.06

but only for the criterion proposed by Krigbaum and Wall. In the case of Garcia et al. [5], the Ch I/HPAM mixtures satisfy this criterion for all of the selected systems.

For the system of Ch II/HPAM mixture solutions, from the values of  $\Delta b_m$  and  $\Delta[\eta]$  parameters which are shown in **Table 2**, it can be suggested that the Ch II/HPAM mixtures are miscible over all of the composition ranges studied, as  $\Delta b_m > 0$  and  $\Delta[\eta] < 0$ . The miscibility criteria are satisfied. Thus, the miscibility of Ch II with HPAM is better than that of Ch I/HPAM. It is well known that the polymers with relatively the same molecular weight tend to be more miscible [13]. This may indicate the influence of the molecular weight of Ch on the miscibility of polymeric components.

## 4. Conclusions

In this paper, the miscibility of dilute aqueous Ch I/HPAM and Ch II/HPAM mixture solutions were investigated. The two different criteria to estimate the polymer-polymer miscibility in dilute solution, as proposed by Krigbaum and Wall [4] and Garcia et al. [5], were considered. Studies of the hydrodynamic properties of the solutions of mixtures indicated that the satisfaction of the miscibility criterion depended on the definition of the ideal parameter value. If the parameter value was defined according to Garcia et al. [5], the investigated mixtures of ChA/HPAM satisfied the miscibility criterion.

## 5. References

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