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Thermodynamics of complex formation of polyacrylic acid with poly(*N*-vinyl-2-pyrrolidone) and chitosan

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Summary

Interpolymer complexing of poly(acrylic acid) (**PAA**) with poly(N-vinyl-2-pyrrolidone) (**PVP**) as well as with chitosans (**CHI**) of various chain lengths was studied at different temperatures by pH measurements. The degree of conversion *(θ)*, the complex stability constant, *K*, and the thermodynamic parameters of these reactions were evaluated. Complexing proceeds cooperatively in both systems and values of θ near unity are obtained for the higher molecular weight samples. The variation of *K* with θ for the **PAA-CHI** system indicates that this complex comprises long sequences of bound pairs of monomer units.

Introduction

Polymers exhibit a high tendency to interact forming interpolymer complexes giving rise to supramolecular structures. Interactions between macromolecules constitute the basis of many biological reactions occurring in living organisms. They provide also a route to the preparation of novel polymeric materials displaying physical properties different of the individual constituent macromolecules. As a result, in the last years considerable studies have been devoted to the elucidation of the nature of these interactions as well as to the evaluation of the physical properties of the resulting materials (1-3)

Interpolymer complexes are often classified according to the nature of their interactions such as: charge transfer or coordination complexes; stereocomplexes resulting from van der Waals forces; hydrogen bonded complexes, and polyelectrolyte complexes (1).

In the present study we report on the thermodynamics of two interpolymer complexing reactions differing in the nature of the macromolecular interactions: the reaction of **PAA** with **PVP**, where complexation occurs through hydrogen bonds, and the interpolyelectrolyte reaction between **PAA** and **CHI**, which is electrostatic in character.

Experimental

PAA ($M_V = 2.9 \times 10^5$) was obtained by free radical polymerization at 70°C in an inert atmosphere using dioxane as solvent and benzoyl peroxide as initiator. The product was purified by three successive precipitations in toluene and dried. **PVP** samples, **PVP-4** ($M_V = 3.5 \times 10^4$) and **PVP-6** ($M_V = 1.2 \times 10^6$), were used as supplied by Aldrich.

Chitosan **CHI-1** (D.D. = 79.9% determined by ^{1}H-nmr, $M_V = 2.3 \times 10^5$) was obtained from shells of lobsters (*Panulirus argus*) and purified as described elsewhere (4). Chitosans **CHI-2** ($M_V = 1.1 \times 10^5$) and **CHI-3** ($M_V = 8.5 \times 10^4$) were obtained by hydrolysis of **CHI-1**

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with nitrous acid by the method described by Allan and Peyron (5). The molecular weights of chitosan samples were determined at 25°C in the solvent system 0.2 mol.L^{-1} sodium acetate/0.3 mol.L^{-1} acetic acid, proposed by Rinaudo *et al.* (6).

The pH measurements of the aqueous solutions of the polyacid or the complex were carried out in a thermostated cell with temperature control (± 0.5°C) in a nitrogen atmosphere using a digital PRÄCITRONIC MV-870 pH-meter with a Philips CE-1 electrode, with an error of 0.02 pH units. In all cases the total concentration of carboxylic groups in the solution was 5×10^{-3} mol.L^{-1}.

Results and discussion

Complexes by hydrogen bonding

Complexation of **PAA** and **PVP** by hydrogen bonding has been reported by different authors (7-10). The relevant equilibrium processes involved in this interaction are the complexation reaction itself and the dissociation of the polyacid:

$$\begin{array}{ccccc} \sim\sim COOH & + & O=\sim\sim & \overset{K}{\rightleftharpoons} & \sim\sim COOH\cdots O=\sim\sim \\ C_0\,(1\text{-}\theta) & & C_0\,(1\text{-}\theta) & & C_0\,\theta \end{array} \tag{I}$$

$$\begin{array}{ccccc} \sim\sim COOH & \overset{K_d}{\rightleftharpoons} & \sim\sim COO^- & + & H^+ \\ C\,(1\text{-}\alpha) & & C\,\alpha & & C\,\alpha \end{array} \tag{II}$$

where θ is the degree of conversion, defined as the fraction of bonded carboxylic groups, K is the stability constant of the complex, α is the degree of dissociation of the polyacid, and K_d is its apparent dissociation constant.

It can be readily shown that if one considers that K_d does not vary appreciably with complexing, the degree of conversion can be calculated as:

$$\theta = 1 - \left(\frac{[H^+]}{[H^+]_0} \right)^2 \tag{1}$$

where $[H^+]$ and $[H^+]_0$ are the hydrogen ion concentrations in presence and absence of **PVP**, respectively. The stability constant of the complex can then be calculated as:

$$K = \frac{\theta}{C_0(1-\theta)^2} \tag{2}$$

where C_0 is the concentration of **PAA**.

The values of θ and K of **PAA-PVP** complexes for two **PVP** samples with different molecular weights are given in Table 1. It can be observed that very high values of θ are obtained in the whole temperature interval studied, with higher values corresponding to higher

*Table 1. Degree of linkage and stability constants of **PAA-PVP** complexes at different temperatures.*

		T (°C)						
		34.2	41.1	47.6	53.6	58.6	65.3	71.0
PVP-4	θ	0.79	0.86	0.88	0.88	0.88	0.89	0.90
	K (L.mol^{-1})	4 000	8 950	14 230	14 290	14 230	15 070	18 000
PVP-6	θ	0.91	0.91	0.93	0.95	0.96	0.96	0.96
	K (L.mol^{-1})	25 020	25 020	34 560	65 200	120 000	120 000	120 000

molecular weight **PVP**. The values obtained are in good agreement with those reported by Osada for the systems poly(methacrylic acid)-poly(ethylene glycol) (**PMAA-PEG**), **PMAA-PVP** and **PAA-PEG** (11,12).

When comparing the complexing systems **PMAA-PEG** and **PAA-PEG**, Osada (11) found out that θ was higher for **PMAA** than for **PAA** complexes. The higher complexing power of **PMAA** was explained in terms of hydrophobic interactions between the α-methyl groups of **PMAA** and the two -CH_2- units in **PEG**. These authors used **PEG** samples with molecular weights ranging from 200 to 20,000. The stronger hydrophobic interactions in the **PMAA-PVP** complex as compared with the **PAA-PVP** system is manifested by the lower stability of the latter in organic solvents (13). However, the values of θ obtained in the present study for the **PAA-PVP** system do not differ appreciably with those obtained for **PMAA-PVP** complexes by Osada (11), which indicates that for high enough molecular weights the cooperativity of the reaction between **PAA** and **PVP** provides the necessary stabilisation to bring complexing in water almost to completion.

The temperature dependence of the stability constant of **PAA-PVP** complexes is shown in Figure 1. With these data the thermodynamic parameters of complexation can be evaluated using the well known thermodynamic relationships: $\Delta G^o = - RT \ln K$, $\Delta H^o = - R\, d \ln K / d\, (1/T)$ and $\Delta S^o = (\Delta G^o - \Delta H^o)/T$.

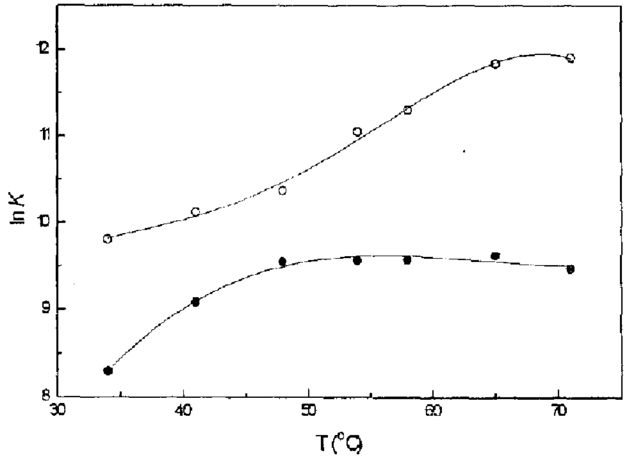


Figure 1. *Temperature dependence of the stability constant for the PAA-PVP complexes.*
(●) *PAA-PVP-4*; (o) *PAA-PVP-6*

The thermodynamic parameters thus determined include contributions from hydrogen bonding, solvent interactions, conformational changes and hydrophobic interactions, among others. As it can be seen in Figures 2 and 3, both ΔH^o and ΔS^o decrease almost monotonically as the temperature increases, the temperature dependence being much more pronounced for the lower molecular weight **PVP**. This is not surprising, since for the higher molecular weight **PVP** a very high degree of conversion is already attained at 34°C.

Since negative values are to be expected for ΔH^o of hydrogen bonds, the positive values obtained are to be interpreted in terms of hydrophobic interactions and conformational changes produced as a result of complexing. Positive values of ΔS^o in aqueous systems indicates the release of water during complex formation (12).

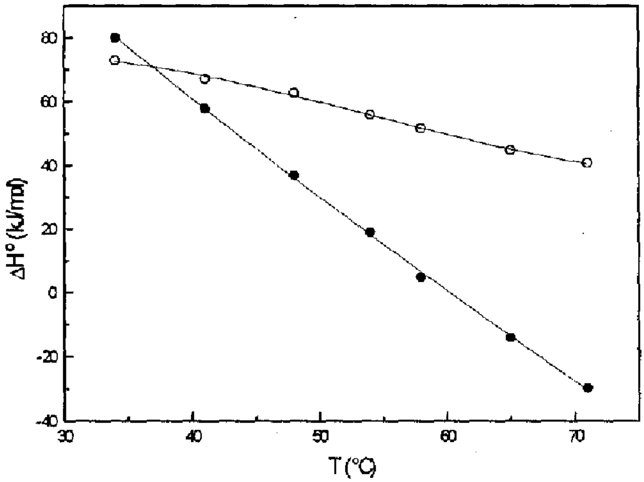


Figure 2. *Standard enthalpy change as a function of temperature for the PAA-PVP complexes.* (●) *PAA-PVP-4;* (o) *PAA-PVP-6*

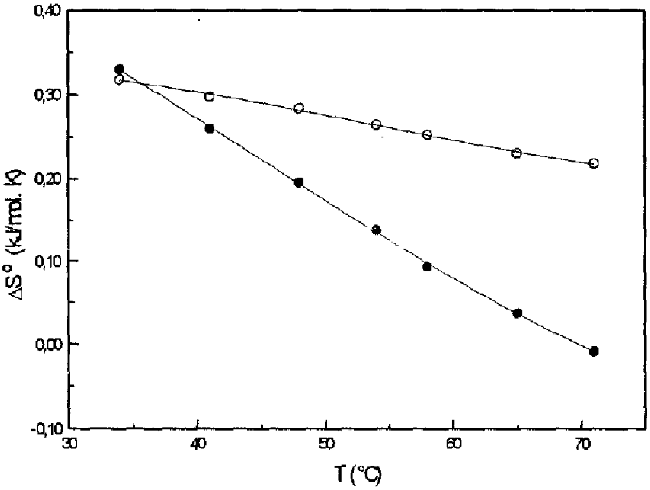
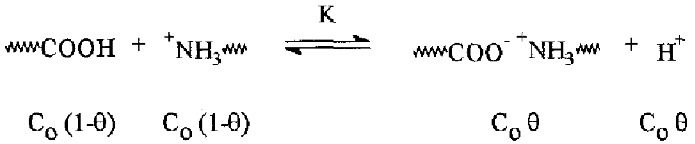


Figure 3. *Standard entropy change as a function of temperature for the PAA-PVP complexes.* (●) *PAA-PVP-4;* (o) *PAA/PVP-6*

Complexes by reaction between polyelectrolytes

The interpolyelectrolyte reaction of **PAA** and chitosan hydrochloride was studied by mixing equimolar quantities of the polyacid and **CHI**. Complex formation proceeds according to the following reaction:



$$\begin{array}{cccc} \sim\!COOH + {}^{+}NH_3\!\sim & \xrightleftharpoons{K} & \sim\!COO^{-}\,{}^{+}NH_3\!\sim + H^{+} \\ C_0(1\text{-}\theta) \quad C_0(1\text{-}\theta) & & C_0\theta \quad C_0\theta \end{array}$$

(III)

Since this reaction is accompanied by release of hydrogen ions, the degree of conversion θ, expressed as the ratio of the concentration of interchain salt bonds formed, C_k to the initial concentration of any of the polyelectrolytes C_O, can be assessed by means of the simple equation:

$$C_k = C_0\theta = [H^+] - [H^-]_0 \tag{3}$$

where $[H^+]$ and $[H^+]_0$ are the hydrogen ion concentrations in presence and absence of **CHI**, respectively. The complex stability constant, K, can then be evaluated as:

$$K = \frac{\theta^2}{(1-\theta)^2} \tag{4}$$

The values of θ and K of **PAA-CHI** complexes at various temperatures are reported in Table 2. It can be seen that for the complexes prepared with the lower molecular weight chitosans, **CHI-2** and **CHI-3**, the degree of conversion of the reaction is low and increases only slightly with the increase in temperature. In contrast, for the higher molecular weight chitosan sample, **CHI-1**, there is a substantial increase in θ as temperature increases, going from 0.17 at 34°C to 0.78 at 71°C. The dependence of complex formation on the chain length of the polyelectrolyte components reflects the cooperativity of this reaction. The above results indicate that the chain dimensions of samples **CHI-2** and **CHI-3** are near the critical chain length for complex formation.

Table 2. Degree of linkage and stability constants of PAA-CHI complexes at different temperatures.

		T (°C)						
		34.2	41.1	47.6	53.6	58.6	65.3	71.0
CHI-1	θ	0.17	0.23	0.28	0.40	0.50	0.62	0.78
	K	0.04	0.09	0.16	0.44	0.92	2.77	12.57
CHI-2	θ	0.10	0.13	0.17	0.19	0.24	0.31	0.36
	K	0.01	0.02	0.04	0.06	0.10	0.21	0.33
CHI-3	θ	0.08	0.11	0.14	0.16	0.19	0.24	0.28
	K	0.01	0.02	0.03	0.04	0.06	0.10	0.16

From the values of the stability constants obtained at different temperatures the thermodynamic parameters (ΔG^O, ΔH^O and ΔS^O) can be calculated as before. The temperature dependence of ΔH^O and ΔS^O are shown in the diagrams of Figures 4 and 5, respectively. It can be appreciated that whereas for the complexes formed with the lower molecular weight chitosan samples, **CHI-2** and **CHI-3**, there is only a small variation of ΔH^O and ΔS^O with temperature, for the higher molecular weight chitosan sample, **CHI-1**, there is a sharp increase in both, ΔH^O and ΔS^O with increasing temperature as the result of the increase in θ with T in this temperature interval. This behaviour is a typical expression of cooperativity in polyelectrolyte reactions. The values of ΔS^O are similar to those of the **PAA-PVP** system, but the values of ΔH^O are much higher for the **PAA-CHI** complexes because of the different nature of the interactions in both systems.

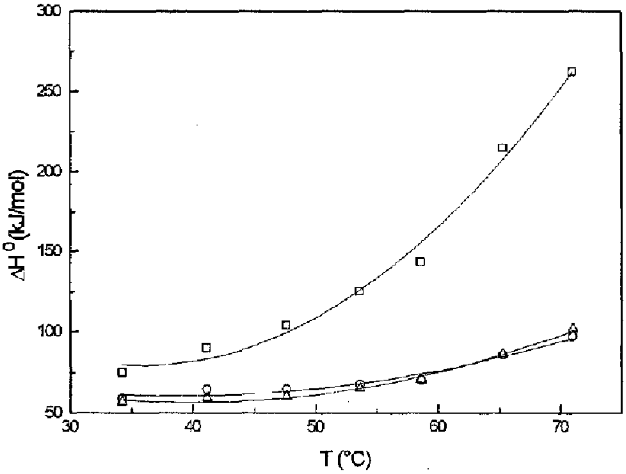


Figure 4. *Standard enthalpy change as a function of temperature for the PAA-CHI complexes.* (□) *PAA-CHI-1*; (o) *PAA-CHI-2*; (Δ) *PAA-CHI-3*

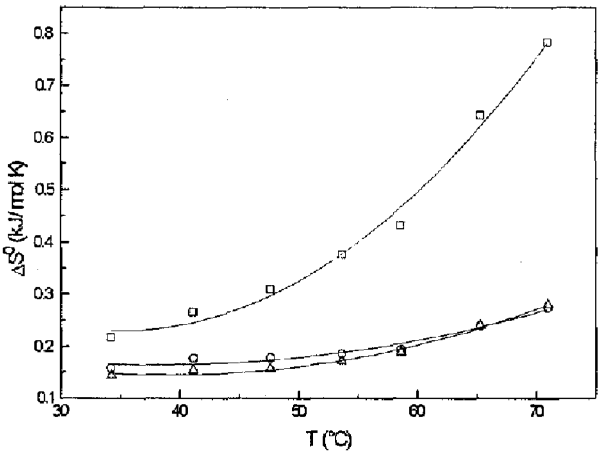


Figure 5. *Standard entropy change as a function of temperature for the PAA-CHI complexes.* (□) *PAA-CHI-1*; (o) *PAA-CHI-2*; (Δ) *PAA-CHI-3*

The calculation of K by equation (4), however, does not allow to analyse the influence of neighbouring functional groups on their reactivity. It assumes that the equilibrium constant for the formation of bond i is the same as for bond i-1. In order to analyse this influence, reaction (III) can be represented as follows:

$$\sim\!\sim\!COOH \overset{K_d}{\rightleftharpoons} \sim\!\sim\!COO^- + H^+ \qquad \text{(IV)}$$

$$\sim\sim COO^- + {}^+NH_3\sim\sim \xrightleftharpoons{K_2} \sim\sim COO^-\,{}^+NH_3\sim\sim \qquad (V)$$

The cooperativity of the reaction can then be interpreted in terms of the variation of K_2 with θ. The existence of cooperativity implies that the reaction constant for the formation of bond i, K_2^i, is higher than the reaction constant for the formation of bond i-1, K_2^{i-1}. It has been pointed out by Zezin and Rogacheva (14) that the magnitude of this variation can have a significant influence on the structure of the complex. If $K_2^i >> K_2^{i-1}$ the complex will tend to exhibit long sequences of consecutive bound pairs. Otherwise the complex will tend to form alternating short segments of bound and unbound sequences. Lutzenko *et al.* (15) showed that this effect can be adequately quantified by expressing K_2 as $K_2 = K_2^0 \exp^{-\varphi(\theta)}$ where $\varphi(\theta)$ is an arbitrary function, chosen so that $\varphi(\theta) = 0$ at $\theta = 0$. In fact they showed that $\varphi(\theta)$ can be adequately described by the linear relationship $\varphi(\theta) = m\theta$, and K_2^0 being the equilibrium constant for the formation of the first interchain bond. Therefore it can be readily shown that the variation of the equilibrium constant K $(= K_d K_2)$ with the degree of conversion θ is given by:

$$\ln K = \ln(K_d \cdot K_2) = \ln(K_d \cdot K_2^0) - m\theta \qquad (5)$$

The logarithmic diagram representing the variation of the equilibrium constant K for the reaction of **PAA** with **CHI** with the degree of conversion θ for the **PAA-CHI** system is represented in Figure 6. There is a linear dependence of ln K on θ in the interval $0.2 < \theta < 0.9$. From the slope of this line, the value of m was evaluated, and found to be $m = -9.07$. This large negative value of m implies that for the reaction between **PAA** and **CHI** K_2 increases markedly with the increase in θ, and the formation of subsequent contacts between the macromolecules is favoured. In other words, the resulting polyelectrolyte complex consists of long sequences of bound pairs of repeat units.

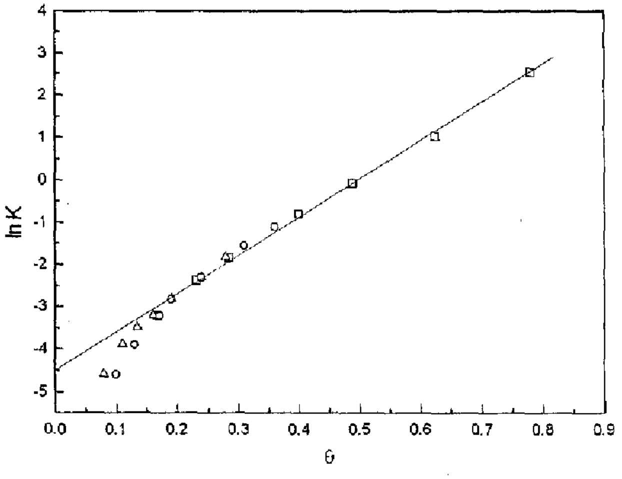


Figure 6. *Linear relationship between the stability constant (K) and the degree of conversion (θ) for the PAA-CHI complexes (the symbols used are identical to those in Figs. 4 and 5).*

Conclusions

Complexing of **PAA** with **PVP** and **CHI** proceeds by a cooperative process. Cooperativity allows the attainment of conversion degrees near unity for high molecular weight samples of **PVP** or **CHI**. The ΔS^{O} of complexation have similar values for both polymers, but the value of ΔH^{O} is much higher in the case of **CHI**, reflecting stronger electrostatic interactions in the **PAA-CHI** complex as compared with the hydrogen bonding interaction of **PAA-PVP** complexes. The variation of K with θ for the **PAA-CHI** system allows to conclude that this complex comprises of long sequences of consecutive bonds.

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