

Temperature induced confirmation transition of poly(L-lysine)

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It is well known that poly(L-lysine) (PLL) undergoes a sharp transition in aqueous solution, when the electrostatic repulsion along the chain is reduced^{1,2}, e.g. around pH 10. The α -helix of PLL and similar polypeptides is stabilized when the pK of amino groups in the side chains is decreased and the formation of intramolecular hydrogen bonds is facilitated. This is accomplished by lowering water activity on addition of some suitable organic component in solution³⁻⁶. However Barskaya *et al.*⁷ showed that the effect of organic component on the conformational equilibrium of

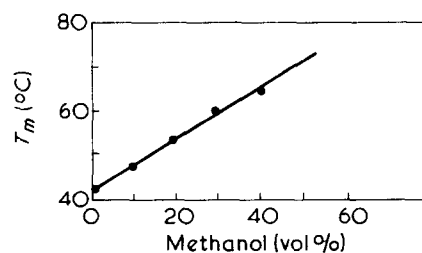


Figure 1 Temperature induced confirmation transition of poly(L-lysine) in a solution of 0.5 mol LiClO_4/l in water-methanol mixtures as a function of methanol concentration

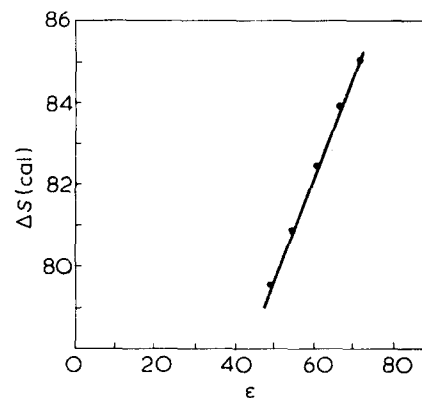


Figure 2 ΔS_{vh} of poly(L-lysine) in water-methanol mixtures (0.5 mol LiClO_4/l) depending on the dielectric constant of the solvent

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PLL is very complicated and does not merely change the dielectric constant of the medium.

The present note is concerned with the optical rotatory measurements of PLL in water-methanol, water-dioxane and water-N-methylformamide mixtures containing 0.5 mol LiClO_4/l . Optical rotation measurements were performed with a JASCO model DIP-SL automatic polarimeter with quartz cells at the wavelength of 365 nm. The temperature of the solution was kept to within 0.02°C of the desired value by circulating thermostatted water through the jackets surrounding the cell.

Figure 1 shows a plot of specific rotation against temperature for PLL. The transition temperature, T_m , is shifted linear to higher values as the methanol content increases. On recalling the Zimm and Bragg relation⁸, namely, $T_m = \Delta H_{vh}/\Delta S_{vh}$, it can be concluded that ΔS_{vh} decreases with increasing alcohol content. This fact may be explained by the decreasing dielectric constant (d.c.) of the medium because the transition in the system under study is due to the repulsion of the charged side chains after dissociation of the complex $\text{PLL}-\text{ClO}_4^-$. The d.c. of the medium plays an important role on the confirmation above T_m because the repulsive forces depend on $1/\epsilon$. With a decreasing d.c. the repulsion of the side chains becomes stronger and stronger and the degree of freedom becomes lower and lower which is equivalent to a decrease in entropy as shown in Figure 2. Very similar results are obtained in water-dioxane mixtures (Figure 3).

It is expected that in a medium of a higher d.c. value than water, T_m is shifted to lower values. This can be proved experimentally by using water-methylformamide (MFA) mixtures; because of the extreme high value of d.c. of MFA (177d, $+20^\circ\text{C}$). In Figure 4 it is shown that T_m indeed is lowered with increasing d.c.

A full account of this work will be published later.

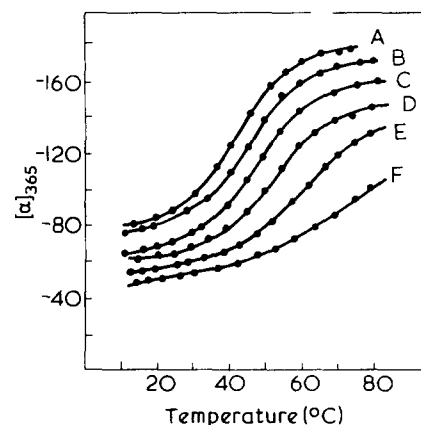


Figure 3 Temperature induced confirmation transition of poly(L-lysine) in 0.5 mol LiClO_4/l containing water-dioxane mixtures; $[\alpha]_{365}/T$. A, 10%, B, 20%, C, 30%; D, 40%; E, 50%; F, 60%

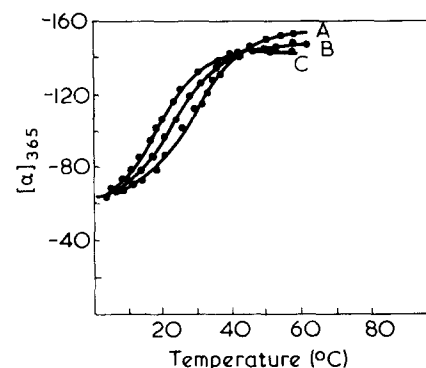


Figure 4 Temperature induced confirmation transition of poly(L-lysine) in N-methylformamide-water mixtures containing 0.5 mol LiClO_4/l . $[\alpha]_{365}$ as $f(T)$. A, 20% Methylformamide; B, 30% methylformamide; C, 40% methylformamide

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