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V. P. Privalko^a; M. V. Buhmistr^a; Yu. S. Lipatov^a

^a Institute of Macromolecular Chemistry, Academy of Sciences of Ukraine, Kiev, USSR

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Thermodynamic Properties and Flow Behavior of Polyionene Solutions

V. P. PRIVALKO, M. V. BUHRMISTR and YU. S. LIPATOV

Institute of Macromolecular Chemistry, Academy of Sciences of Ukraine, 252160, Kiev, USSR

The effect of temperature, chain length and concentration on the conformational state and intermolecular interactions of two model polyionenes in water solutions is discussed.

KEY WORDS Polyionene solutions, rheology, conformational states.

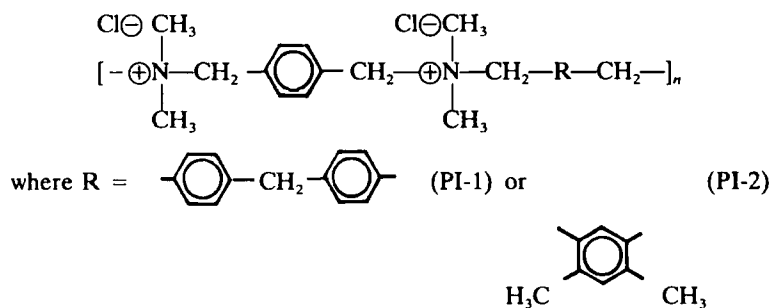
INTRODUCTION

Polyionene (PI) is a generic name for a special class of polyelectrolytes with positive charges in the chain backbone and either equal (symmetrical PI) or unequal (unsymmetrical PI) spacings between charges.¹ In recent years a renewed interest in PI's was stimulated by novel data on their behavior both in the bulk state^{2,3} as well as in solution.^{4–6} For example, as can be inferred from the viscosity studies of PI solutions in water and in mixed solvents,^{5,6} the structure of the solvent is changed on addition of even very small amounts of PI. It is thus the purpose of the present paper to elucidate the effect of temperature, chain length and concentration on the conformational state and intermolecular interactions in water solutions of two model PI's.

EXPERIMENTAL

Materials

Two model unsymmetrical PI's of the general structure



were synthesized by methods described in detail elsewhere.⁷ Polymers were recovered from reaction medium by precipitation with acetone and dried in vacuum at 323 K for several hours to constant mass. Z-Average molecular masses (M_z), determined from sedimentation data by ultracentrifuge model MOM-3180, were 17.9×10^3 (PI-1) and 8.4×10^3 (PI-2).

Methods

Integral heats of solution (ΔH_s) and dilution (ΔH_d) were measured (with mean error 1.0–1.5%) with the aid of a home-made differential calorimeter on diathermal cells with an in-built microstirrer and calibrated electric heater.⁸ Most of the data presented in the subsequent discussion are the mean values taken from two or three independent measurements.

Viscosities of dilute solutions were measured (with mean error 0.5–1.0%) with an Ubbelohde-type viscometer ($t = 150$ sec for water at 298 K); at higher concentrations a constant shear rate-type rotational instrument, model RHEOTEST-2.1, with a double-cylinder geometry, was used (mean error on the order of 5%).

RESULTS AND DISCUSSION

Thermodynamic Properties

As can be seen from Figure 1, all isothermal plots of concentration dependence of specific (i.e., per unit mass of a polymer) heats of solution, ΔH_s , exhibit minima, the positions of which are functions of temperature. The patterns of temperature dependence of ΔH_s at constant mass fraction of a polymer, W_2 , are drastically different in temperature intervals below and above 303 K, namely (see Figure 2): at $T < 303$ K the *exothermic* ($\Delta H_s < 0$) heat effects increase linearly with temperature, whereas at $T > 303$ K a sudden transition to *endothermic* ($\Delta H_s > 0$) effects is observed. The dilution phenomena at different initial concentrations of PI in solution (Figure 3) are also endothermic ($\Delta H_d > 0$).

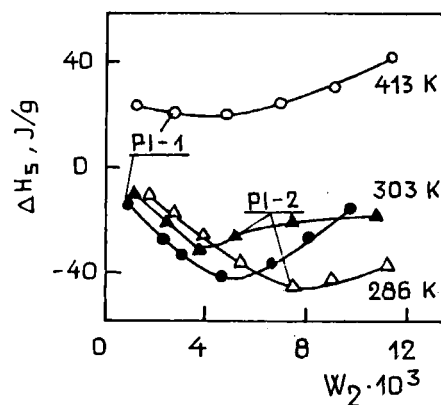
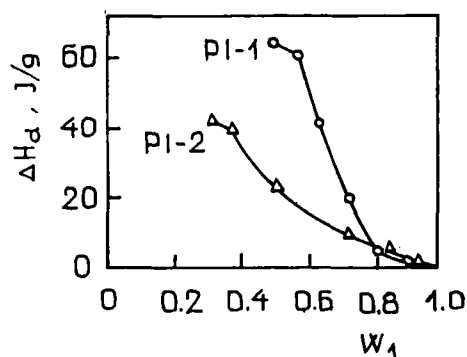
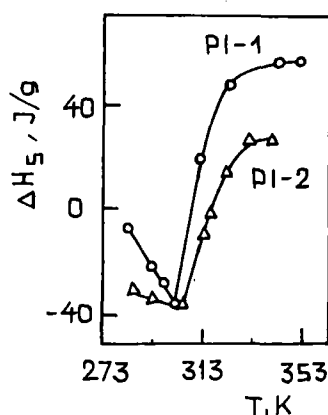


FIGURE 1 Concentration dependence of heats of solution.

FIGURE 2 Concentration dependence of heats of dilution at $T = 295$ K.FIGURE 3 Temperature dependence of heats of solution at $W_2 = 2.3 \cdot 10^{-3}$.

- | | |
|----------------------|--|
| $\Delta H^V > 0$ | Dissociation of van der Waals bonds between PI chains; |
| $\Delta H^E < 0$ | Dissociation of electrostatic bonds in PI; |
| $\Delta H^P > 0$ | Breakdown of the structure of bulk water; |
| $\Delta H^{H^+} < 0$ | Interactions of hydrophilic groups of PI with water (hydrophilic hydration); |
| $\Delta H^{H^-} < 0$ | Aggregation of water molecules around hydrophobic groups of PI (hydrophobic hydration) |

FIGURE 4 Scheme 1: Contributions to the heat of interaction of polyionenes with water.

The above data will be analyzed within the framework of the following structural considerations. Macromolecules of bulk PI obtained by precipitation from a good solvent (reaction medium), are in a coiled conformation which satisfies the conditions of both screening of intramolecular repulsion between charged atoms and saturation of all possible kinds of intermolecular bonds. Obviously, as more and more solvent is added to polymer, both local and overall concentrations of counterions will be continuously decreasing ("intermolecular dilution"), while local (intramolecular) concentration of positive charges in the chain will remain unchanged. Thus, in the "infinitely dilute" solution regime the effect of intramolecular screening vanishes and the macromolecules undergo a transition into extended

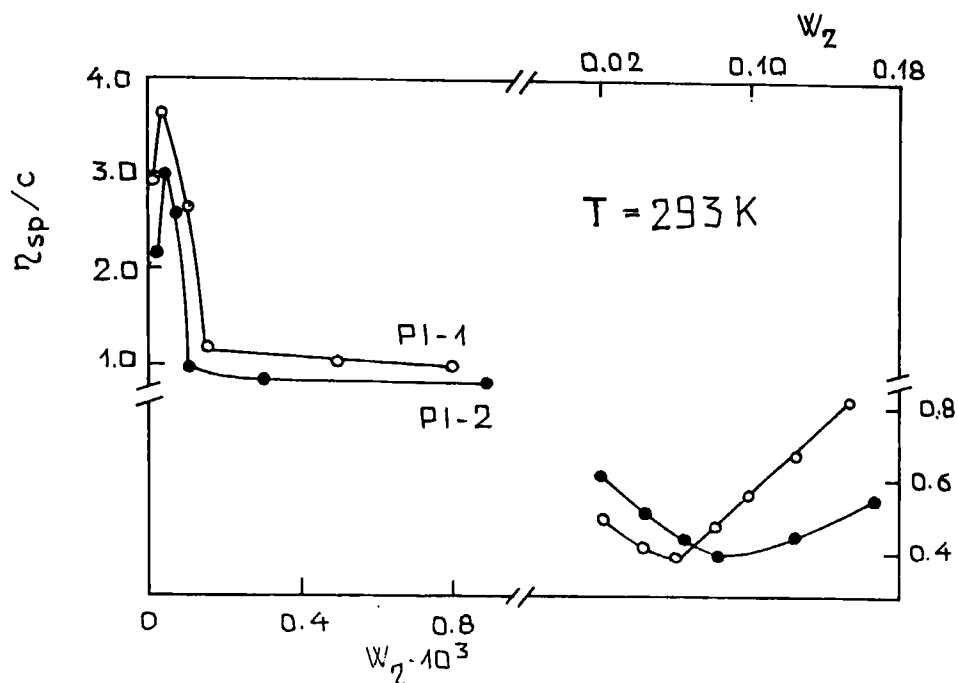
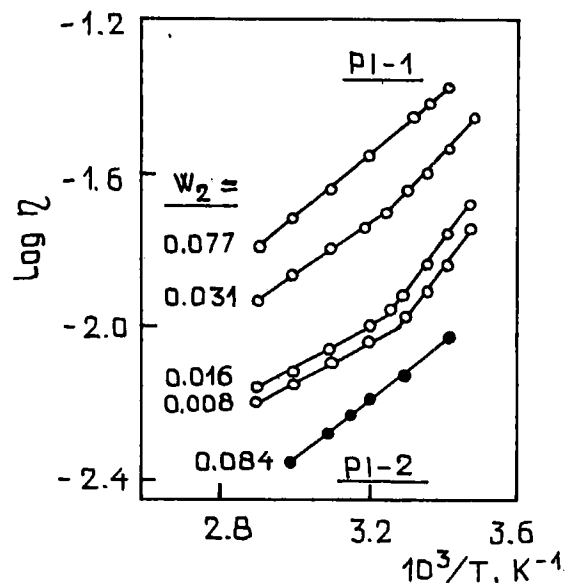
FIGURE 5 Concentration dependence of reduced viscosity at $T = 295 \text{ K}$.

FIGURE 6 Temperature dependence of shear viscosity at indicated polymer concentrations.

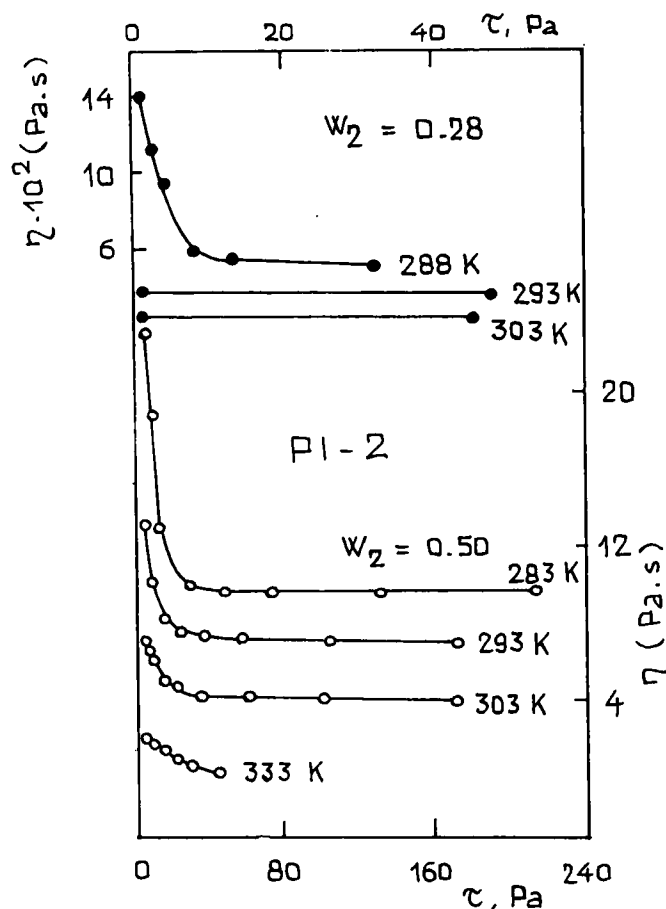


FIGURE 7 Dependence of shear viscosity on shear stress at indicated temperatures and concentrations.

conformation (effect of polyelectrolyte swelling) which corresponds to a maximum possible distance between charged atoms.⁹ Transition to a “semi-dilute” solution regime would lead to the onset of electrostatic interactions between extended chains whereas further increase of polymer concentration (i.e., transition to a “concentrated” solution regime) would strengthen the effect of interchain screening of electrostatic interactions and, consequently, induce the transition of macromolecules into more coiled conformation.^{10,11}

Using Scheme 1 (Figure 4) as a starting point for a qualitative discussion of calorimetric data (Figures 1–3) it may be argued that the exothermic pattern of dissolution of both PI’s below 303 K (Figures 1 and 2) is the manifestation of a dominant contribution of exothermic effects ΔH^E , ΔH^{H+} , ΔH^{H-} as compared to ΔH^V and ΔH^D , which accompanied the transition of PI chains from the bulk state into dilute solution. The more exothermic pattern of dissolution at increased dilution (Figure 1) may be explained by a smaller contribution of ΔH^D , whereas subsequent (at $W_2 < 4 \cdot 10^{-3}$) decrease of “exothermicity” may be explained by a lower degree of intermolecular association of extended PI chains (and, correspond-

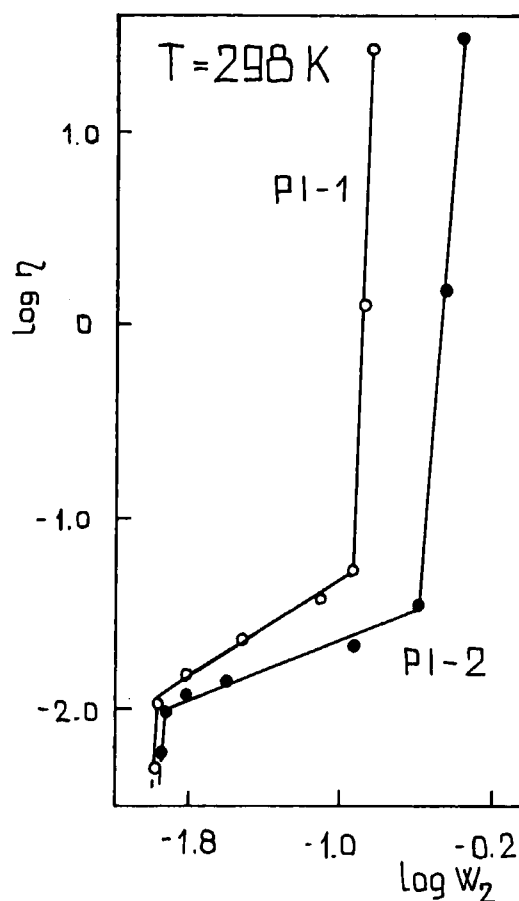


FIGURE 8 Concentration dependence of shear viscosity at $T = 298$ K and constant molecular mass.

ingly, by a smaller contribution of ΔH^{H^+} , ΔH^{H^-}) at a negligibly small contribution from the effect of breakdown of the structure of bulk water (ΔH^D).

Negligible values of the heats of dilution ΔH_d in the range of fairly small concentrations ($W_2 < 0.05$) of both PI's in initial solutions (Figure 3) are also an indication of a negligible contribution of ΔH^D to interactions of water molecules with individual macromolecules of PI in an extended conformation. Onset of the endothermic heats of dilution at higher initial concentrations ($W_2 > 0.05$) is likely a manifestation of a transition to the semi-dilute solution regime with increased contribution from ΔH^D , while subsequent accelerated rise of ΔH_d at $W_2 > 0.20$ is presumably due to a transition to the concentrated solution regime where a continuous gain of endothermic ΔH^D and ΔH^V effects exceeds by far the contributions of exothermic ΔH^E , ΔH^{H^+} and ΔH^{H^-} processes.

In conclusion, a discussion of the temperature effect on the energetics of PI dissolution (Figure 2) is in order. Assuming that the final concentration, $W_2 = 2.3 \cdot 10^{-3}$, corresponds to the dilute solution regime (see above), it may be argued that the observed sudden change of the pattern of temperature dependence of ΔH_d at $T = 303$ K is a result of a structural transformation in either a solute phase (PI)

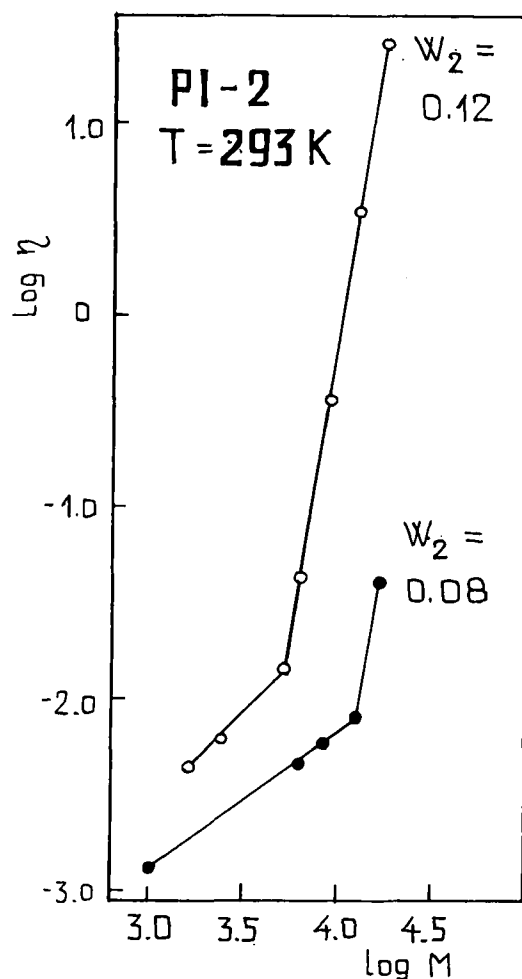


FIGURE 9 Molecular mass dependence of shear viscosity of PI-I solutions at $T = 298$ K and constant concentration.

or a solvent phase (water). As follows from Scheme 1, at low polymer concentration the major contributions to ΔH_s are provided by two exothermic hydration processes, ΔH^{H^+} and ΔH^{H^-} , and by an endothermic process of water structure breakdown, ΔH^D . Therefore, positive slopes on the ΔH_s versus T plots (in other words, positive values of the apparent heat capacity of solution process, $C_{p,s} = d\Delta H_s/dT$) above $T = 303$ K may be interpreted as qualitative evidence of coiled conformation of PI chains, an arrangement which discourages interactions of both hydrophilic and hydrophobic groups of PI with water molecules (hence, the contributions of ΔH^{H^+} and ΔH^{H^-} are small) but induces the change of water structure (the contribution of ΔH^D dominates). On the other hand, a negative value of $C_{p,s}$ at $T < 303$ K indicates easier access of water molecules to hydrophilic and hydrophobic sites in PI chains as a result of transition of the latter into more extended conformation (hence, contributions of ΔH^{H^+} and δH^{H^-} increase) which perturbs the water structure less (contribution of ΔH^D decreases).

A similar conclusion may be reached starting from completely different assumptions. It can be easily shown that the contour distance A between charges in PI chains ($A = 0.7$ nm and $A = 0.6$ nm for PI-1 and PI-2, respectively) are of the same order of magnitude as the characteristic Bjerrum length l_B ⁹ for the formation of ionic pairs in water at $T = 303$ K ($l_B = e^2/DkT = 0.7$ nm), but is smaller than the effective thickness of the screening ionic atmosphere¹¹: $(k'')^{-1} = (4\pi AW_2)^{-2} = 6.5$ nm for PI-1 and 6.0 nm for PI-2 where $e^2 = 2.3 \cdot 10^{-26}$ J·cm is the square of electron charge, $D = 78.5$ is the dielectric permittivity of water,^{12,13} and k is Boltzmann's constant). It follows that the electrostatic chain persistence length,¹¹ $L^E = l_B/4(k'')^2A^2$, with values of 15 nm for PI-1 and 18 nm for PI-2, is larger than the thickness of the screening ionic layer at $T = 303$ K. Taking into consideration that cooling to $T = 278$ K is accompanied by a nearly 1.5-fold drop of dielectric permittivity of water,¹⁴ it can be shown that this effect should lead to a corresponding increase of l_B up to 1 nm, and an increase of electrostatic chain persistence length up to 21.5 nm for PI-1 and 25.7 nm for PI-2.

Judging by the above estimates, in the temperature interval above 303 K the macromolecules of PI's in dilute water solutions are in a coiled state which is favorable for the endothermic pattern of breakdown of the structure of bulk water. Cooling of such dilute solutions below 303 K results in the transition of PI chains into a more extended conformation which strengthens the contributions from exothermic processes of hydrophilic and hydrophobic hydration and minimizes the effect of breakdown of the structure of bulk water.

Flow Behavior

As can be seen from Figure 5 (left-hand side), both PI's exhibit a classical polyelectrolyte behavior,^{4,5,9} namely, at extremely small polymer concentrations further dilution leads first to the drastic increase of reduced viscosity, η_{sp}/C , followed by a substantial drop of this viscosity below the first "critical" concentration, $W_2^{1''} = 5 \cdot 10^{-5}$, which marks the transition from the "dilute" to "extremely dilute" solution regime. The former phenomenon may be explained by chain extension as a result of reduced shielding of positive charges in the chain backbone by the counterions (effect of intramolecular repulsion between identical charges), while the latter one simply reflects the reduced interactions between extended macromolecules (intermolecular effect).

As the concentration grows (Figure 5, right-hand side), the reduced viscosity slightly decreases (presumably because macromolecules gradually become less extended) up to the second "critical" concentration, $W_2^{2''} =$ (with values of 0.05 and 0.08 for PI-1 and PI-2, respectively), and then starts to increase again (due to the onset of aggregation of less extended PI chains). It is pertinent to remark here that it is only below $W_2^{2''}$ that one observes the breaks at about $T = 303$ K on the semi-logarithmic plots of shear viscosity of PI-1 solutions against reciprocal temperature (Figure 6). Recalling the data on the temperature dependence of heats of solution (Figure 4) it may be argued that at $W_2 < W_2^{2''}$ (i.e., in the "dilute" solution regime) the lower activation energies for viscous flow above $T = 303$ K ($\Delta E_v/k = 1.3 \times 10^3$ K) refer to the flow of coiled, individual PI-1 chains, whereas more than a two-

fold increase of $\Delta E_v/k$ below $T = 303$ K (up to 3.1×10^3 K) reflects the transition of PI-1 macromolecules into a more extended conformation.

On further increase of W_2 , the breaks on the above plot become less pronounced and vanish completely in the "semi-dilute" solution regime (above W_2^{2c}) for both PI's, with the corresponding activation energies being $2.1 \cdot 10^3$ for PI-1 and $1.8 \cdot 10^3$ K for PI-2 (Figure 6). Assuming that viscous flow of aggregates requires higher values of $\Delta E_v/k$, it follows from the data obtained that the flow entities in the semi-dilute solution regime are aggregates of PI chains in a coiled conformation similar to that of individual chains at $T > 303$ K, rather than aggregates of extended macromolecules.

At still higher polymer concentrations ($W_2 > W_2^{3c}$) the non-Newtonian behavior sets in, that behavior being more pronounced at lower temperature (Figure 7). As can be seen from Figure 8, the double logarithmic plots of shear viscosity (at constant shear rate) against polymer concentration consist of two linear portions intersecting at the third "critical" concentration, W_2^{3c} , with values of 0.11 for PI-1 and 0.20 for PI-2. A jump-like increase of the slopes on those plots at W_2^{3c} from 0.5 to 26.0 (PI-1) and from 0.3 to 12.0 (PI-2) is undoubtedly a manifestation of transition to a "concentrated" solution regime, characterized by formation of a continuous network of entangled, coiled macromolecules.

This latter transition to "concentrated" solution regime may be detected not only from $\log \eta$ -versus- $\log W_2$ plots at constant molecular mass, M_2 (Figure 8), but also from $\log \eta$ -versus- $\log M_2$ plots at constant concentration, W_2 . Figure 9 shows that the latter plots also consist of two straight lines intersecting at the "critical" (entanglement) molecular mass, M_2^c . As expected, M_2^c is lower the higher is W_2 , these two quantities being connected by an apparent scaling relationship, $W_2 \propto M_2^{-0.8}$. This result is in a good qualitative agreement with the corresponding theoretical prediction.¹¹

CONCLUSIONS

As follows from the experimental study of thermodynamic properties and flow behavior of water solutions of two model polyionenes, in the "extremely dilute" solution regime below the first "critical" concentration, W_2^{1c} , the macromolecules of both PI's assume the most extended conformation due to the effect of intramolecular repulsion between like charges in the chain backbone. This effect gradually diminishes on transition to the "dilute" solution regime ($W_2^{1c} < W_2 < W_2^{2c}$) since the intramolecular charges of PI's are shielded by counterions, and the chain conformation becomes less extended. Heating the dilute solution above $T = 303$ K makes the individual PI chains assume a coiled conformation as a result of the structural change in bulk water. Intermolecular shielding of PI charges in the "semi-dilute" solution regime ($W_2^{2c} < W_2 < W_2^{3c}$) due to a lateral aggregation of macromolecules also promotes their transition into a coiled conformation. Finally, in the "concentrated" solution regime above the third "critical" concentration, W_2^{3c} , [or, equivalently, above the "critical" molecular mass, $M_2^c = f(W_2)$], the coiled macromolecules form a continuous entanglement network.

It should be remarked here that although the same physical mechanisms were invoked to explain the special features of concentration dependences of both heats of solution and dilution on one hand, and solution viscosity, on the other, the boundaries between different solution regimes deduced from both sets of data did not coincide. Nevertheless, this apparent discrepancy is in fact not too alarming in view of the obviously different sensitivity of both methods to structural changes occurring in the solute and/or in the solvent phase.

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