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Unusual behavior of water soluble polyelectrolyte macromolecules shown by QELS study : is it a property of hydrophobic backbones ?

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Résumé. — Nous avons étudié les aspects dynamiques d'un polyélectrolyte en solution aqueuse, en utilisant la technique de la diffusion quasi-élastique de la lumière. Deux conclusions majeures ont été atteintes pour le cas des solutions sans contre-ions extérieurs et le cas où la force ionique devient importante. Pour le cas sans sel, la dynamique du système est caractérisée par deux modes de fluctuations : un mode coopératif et des fluctuations à longue distance. Ceci reflète une conformation étendue des solutés macromoléculaires. Au contraire, l'augmentation de la force ionique est accompagnée par une importante réduction de la conformation des macromolécules. Un seul mode de fluctuations émerge. Le coefficient de diffusion collectif, qui a aussi été mesuré, ne dépend ni de la concentration du soluté, ni de la force ionique quand cette dernière dépasse une valeur critique faible. Nous attribuons ce phénomène à la prédominance d'interactions hydrophobes, étant donné que les effets d'écrantage réduisent la portée des forces de Coulomb entre les polyions, et à cause de la structure d'hydrocarbure du squelette de polymère.

Abstract. — Using QELS technique we studied the dynamic aspects of a synthetic flexible polyelectrolyte compound in aqueous solutions. By monitoring the ionic strength from very small to high values, we reached two major conclusions. First, in the absence of added electrolyte(s), the polyions are in a « highly » expanded conformation ; the dynamics are characterized by two fluctuation modes : cooperative and long range fluctuations. The addition of NaCl introduces a « sharp » and *a priori* unusual change. The solute macromolecules experience a non gradual change in their conformation, which is directly reflected in their dynamics. The mutual diffusion coefficient, deduced from the only existing decay rate for the correlation function, does not reflect any observable variation with polymer or salt concentration (c_p and c_s respectively), for the values we scanned. We attribute this phenomenon to the rising of hydrophobic interactions, once the shielding of the electrostatic interactions becomes effective at sufficiently high ionic strengths, owing to the hydrocarbon nature of the polyions.

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Introduction.

It has been known that polyelectrolyte solutions experience different behavior depending on whether or not one adds simple electrolyte(s) ions to the system [1-8]. For solutions without externally added counterions, the long range Coulomb repulsive interactions between neighboring charges along one polyion chain impose a local stiffening and, consequently, an expanded conformation to the polyion. This phenomenon is at the origin of the appearance of an « ordered » phase, as was found by small angle neutron and X-ray scattering studies [4-8]. Conversely, the counterion excess in solutions with high ionic strength screens out these repulsive interactions. The screening effects manifest themselves in a gradual change in the solution properties as function of the ionic strength [4-7]. For instance, the « ordered » phase disappears for sufficiently high counterion excess [4]. This is accompanied by a reduction in the chain expansion for flexible polymers. This change in polyion conformation with the addition of ions to the solution has been observed to occur for many polyelectrolyte compounds. Nevertheless, its onset and development vary for different compounds. Many parameters contribute : polyion nature and charge density along the backbone, for instance.

QELS technique has been used by many authors to probe polyelectrolyte solutions properties [9-19]. The diffusion coefficient and its dependence on polymer concentration, molecular weight, macromolecules valence, ionic strength, etc., have been measured. Two diffusion processes were often found for low ionic strength even at small concentrations. Above an ionic strength threshold, only one diffusion coefficient was measured. This coefficient has different types of variation with the ionic strength, depending on the intrinsic properties of the polymer. On one hand, the value measured at zero polymer concentration, D_T^0 , is constant for some biological materials : DNA, BSA, which are ordinarily assumed not to undergo any conformational change as the ionic strength of the solution increases [10-13, 18]. However, for many flexible macromolecules, D_T^0 does change progressively and noticeably with the increase in counterion excess [18, 29]. On the other hand, for finite polymer concentration the diffusion coefficient is found to decrease with increasing c_s for BSA and DNA, but it increases with c_s for κ -carrageenan [12-16].

We present a QELS study, undertaken on a water soluble synthetic polymer compound. The change in solution properties between the salt-free case and the case with added salt is found to occur in an « unusual » manner when compared to previous results reported on polyelectrolyte materials. The present set of data is compared to previous work reported on different compounds as well as other measurements undertaken on this system in a different solvent (methanol) [29].

Experimental section.

It is well known that the time dependent structure factor $S(q, t)$ is non-zero for non homogeneous media, e.g. polymer solutions, in which concentration fluctuations δc occur [20, 21] :

$$S(q, t) = \langle \delta c(q, t) \delta c^*(q, 0) \rangle \quad (1)$$

where $\langle \rangle$ denotes the thermodynamic average over all chains configurations in the sample. The time dependent structure factor could also be written within the framework of Brownian motion governed by the Einstein law for the diffusion process as [20, 21] :

$$S(q, t) = S(q, 0) e^{-\Gamma t} = S(q, 0) e^{-Dq^2 t} \quad (2)$$

where D is the translational diffusion coefficient, q is the scattering wavevector which depends on the scattering angle θ : $q = (4\pi/\lambda)n_s \sin(\theta/2)$; n_s is the solvent refractive index and λ is the wavelength of the incident light. For concentrated polymer solutions, macromolecules interpenetrate and fluctuations become also a cooperative phenomenon. Therefore, $S(q, t)$ could be written as a combination of the two contributions [21]:

$$S(q, t) = S(q, 0) [\alpha e^{-D_C q^2 t} + \beta e^{-D_S q^2 t}] \quad (3)$$

where α and β are two constants which reflect the relative contributions of these two processes, and obey the condition $\alpha + \beta = 1$. D_S and D_C are, respectively, the large scale and the cooperative diffusion coefficients. These two different coefficients are related to two characteristic sizes through the Stokes relation: $D_{C,S} = kT/6\pi\eta_S \xi_H$, S_H , where η_S is the solvent viscosity coefficient, S_H is the large scale size fluctuation (often attributed to the « overall » size of the macromolecule for high concentrations) and ξ_H is the hydrodynamic correlation length or the dynamic blob size [21]. The predominance of one process or the other depends on the time scale measurement: for t small Γ_C is predominant; a combination of both processes is observed over longer time scale.

The QELS experiment provides the normalized intensity autocorrelation function $G^{(2)}(t)$, at a given scattering vector q :

$$G^{(2)}(t) = \frac{\langle I(0)I(0+t) \rangle}{\langle I^2 \rangle} \quad (4)$$

$G^{(2)}(t)$ also reads as:

$$G^{(2)}(t) = a + b |g^{(1)}(t)|^2 \quad (5)$$

where a is the background signal, b is a constant accounting for the detecting optics, and $g^{(1)}(t)$ is the normalized field correlation function directly related to $S(q, t)$ (Eqs. (1) and (2)).

For solutions with homodisperse solute macromolecules in the dilute regime (isolated macromolecules), the autocorrelation function has a simple form:

$$G^{(2)}(t) = a + b e^{-2\Gamma t} \quad (6)$$

where $\Gamma = D_{ef} q^2$ and D_{ef} is the coil mutual diffusion coefficient also accounting for the objects interactions in the solution. However, in polymer solutions macromolecules are always subject to size dispersion, and single exponential form does not provide a good description for the relaxation form of $G^{(2)}(t)$. In practice, cumulants analysis is often used to fit the correlation function:

$$G^{(2)}(t) = a + b e^{At + Bt^2 + Ct^3 + \dots} \quad (7)$$

where, A, B, C, \dots are respectively, related to the first second etc., cumulants [30]. $A = -2\Gamma$ and provides us with D_{ef} . B is related to the variance and so reflects the deviation from a single exponential form. The ratio B/A defines the polydispersity of the measurement.

The cumulants expansion has provided a good fit for the correlation function $G^{(2)}(t)$ for the set of solutions with « high » ionic strength. The polydispersity factor B/A for these systems was found to be about 0.15-0.25 and is considered satisfactory because of the molecular weight distribution [22, 26].

However, for the case of salt-free solutions (or solutions with very low ionic strength), the cumulants expansion does not fit the corresponding correlation function. Two time scale

dynamics occur (Fig. 2b). A double exponential expression is necessary to describe the intensity correlation function decay with time :

$$G^{(2)}(t) = a + b [\alpha e^{-\Gamma_c t} + \beta e^{-\Gamma_s t}]^2 \quad (8)$$

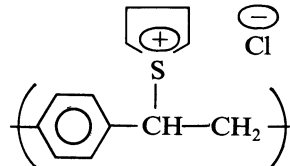
$\Gamma_{c,s}$ are introduced above (Eq. (5)). In practice, the two decay rates are actually extracted through the use of the Laplace inversion of the normalized distribution of decay rates $G(\Gamma)$:

$$g^{(1)}(t) = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma. \quad (9)$$

A plot $G(\Gamma)$ vs. Γ (or $\text{Log } \Gamma$) reflects the correlation function behavior, e.g., $G(\Gamma)$ shows one or more peaks depending on whether or not the field correlation function $g^{(1)}(t)$ has one or more decay rates. The Laplace inversion was done numerically using a computer Vax program : Contin analysis, provided by the computer center at the University of Massachusetts. This analysis has been mostly applied to salt-free solutions. Nonetheless, we checked that for solutions with high ionic strength, $G(\Gamma)$ exhibits one peak and that the corresponding Γ_{av} (average decay rate) provides a value D_{av} for the diffusion coefficient which agrees with D_{ef} extracted from cumulants analysis.

We used a well known photon correlation spectroscopy set-up, i.e., QELS, which has been described previously [30, 31]. The normalized intensity autocorrelation function $G^{(2)}(t)$ is recorded using a photocalorator Langley Ford DM 1096 with 256 channels and 16 channels delayed. We used a He-Ne laser source, $\lambda = 6328 \text{ \AA}$, and an index matching bath for the sample tube [30, 31].

In the present work, the polyelectrolyte compound used is the poly(xylydene tetrahydrothiophenium chloride), described previously, and often identified as the poly (p-phenylene vinylene), PPV, precursor [23-26]. It has the following chemical formula :



This compound has been synthesized in an «unusual manner». The polyions were obtained from anionic polymerization, in water, of the monomer (xylydene tetrahydrothiophenium chloride) ions. The polymer thus obtained is afterwards precipitated in acetone and washed many times with clean deionized water, to eliminate extra free ions. It is then dried under nitrogen atmosphere for several hours. The resulting material is then dissolved in clean double deionized water and used for measurements purpose. To check the purity of salt-free solutions from residual ions, we measured the conductivity : this was found very small : $\sigma \approx 0.04\text{-}0.1 \text{ ms/cm}$ for $c_p < 1 \text{ g/l}$. However, the conductivity reaches a value $\sigma \approx 13 \text{ ms/cm}$ at $c_s \approx 0.01 \text{ M}$ and $c_p = 0.3 \text{ g/l}$. The smallness of this value, in the first case, reflects the purity of the salt-free solutions ; it has a finite value because of the residual contribution of the ions coming from the macromolecules. The solutions were filtered into the sample tube through a millipore filter $0.8 \mu\text{m}$. A smaller hole size filter ($0.45 \mu\text{m}$) is found to alter the solutions. The molecular weight was determined by G.P.C., and checked by light scattering [29] : $M_w = 10^6$ and $(M_w/M_n = 2)$ [26].

The compound is the subject of active interest because of the high electrical conductivity of the final poly (p-phenylene vinylene) product. This last is obtained after elimination of the

sulfonium salt at high temperature. The conductivity reached is about $\sigma = 10^3$ ms/cm, when doped with metal atoms such as arsenic pentafluor (AsF_5) [23-25]. PPV also shows a strong tendency towards crystalline behavior [27, 28].

In aqueous solutions, the high polarity of water molecules is assumed to be strong enough to dissociate chloride ions from the polymer backbone and thus to induce a polyelectrolyte behavior to the solution. Sodium chloride (NaCl), (Fisher Scientific Inc.), was used as a conventional electrolyte. All measurements were made at a constant room temperature of $T \approx 25^\circ\text{C}$.

Results and discussion.

The main point we wish to emphasize is that the salt-free ($c_s = 0$) solutions exhibited fundamentally different behavior from the case of solutions to which salt had been added ($c_s \neq 0$).

The change in solution behavior occurs at different levels. First, the static scattered intensity $I(q, 0)$ is very weak for salt-free solutions. However, it is strongly increased by the presence of a small amount of added NaCl. For instance, the ratio between the scattered intensities in the presence and the absence of salt is about 15 for $\theta = 25^\circ$, $c_p = 1$ g/l and $c_s = 0.10$ M (Fig. 1). This important difference cannot be simply attributed to a higher refractive index increment $(\delta n/\delta c)^2$ in the presence of added salt. The second change in solution behavior concerns the intensity correlation, $G^{(2)}(t)$ curves. This point is discussed separately for both set of solutions.

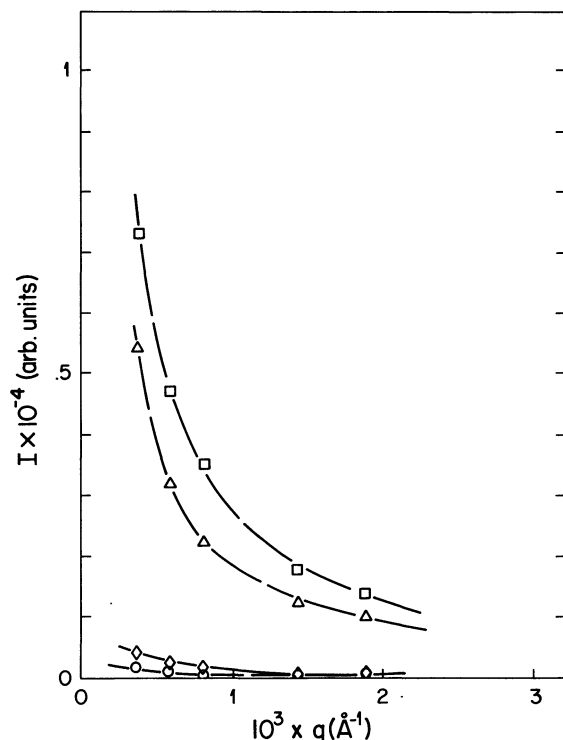


Fig. 1. — Static scattered intensity I (in arbitrary unit) vs. q for different samples : (O) pure water, (◇) salt-free solution at $c_p \approx 1$ g/l, (Δ) Solution with added salt, $c_s = 0.02$ M, $c_p = 1$ g/l, (\square) The same solution with added but not controlled salt : $c_s < 0.3$ M.

a. SALT-FREE SOLUTIONS. — For solutions with no added electrolyte, even though the static scattered intensity is weak, the intensity correlation function does undoubtedly show two

different decay rates Γ_f and Γ_s (Figs. 2a, 3). These decay rates reflect two separate modes of fluctuations called by QELS users, fast and slow modes respectively. The corresponding diffusion coefficients D_C and D_S provide two characteristic sizes ξ_H and S_H , using the Stokes relation (Tab. I). The net distinction between the magnitude of Γ_f and Γ_s (hence

Table I. — Values of the cooperative and large scale diffusion coefficients, D_C and D_S as well as the corresponding sizes ξ_H and S_H for « salt-free » solutions are reported in the first line. The evolution of D_C and D_S with salt concentration are reported in the other lines.

$10^3 \times c_S$ (M)	c_P (g/l)	$10^8 \times D_S$ (cm ² /s)	$10^6 \times D_C$ (cm ² /s)	S_H (Å)	ξ_H (Å)
0	0.1-1	4.30	1.95	565	12
0.5	0.3	5.5	0.12	445	204
2	0.3	~ 4	0.195	610	125
8	0.3	4.5	—	545	—
uncontrolled ~ 100	0.3	4.5	—	545	—

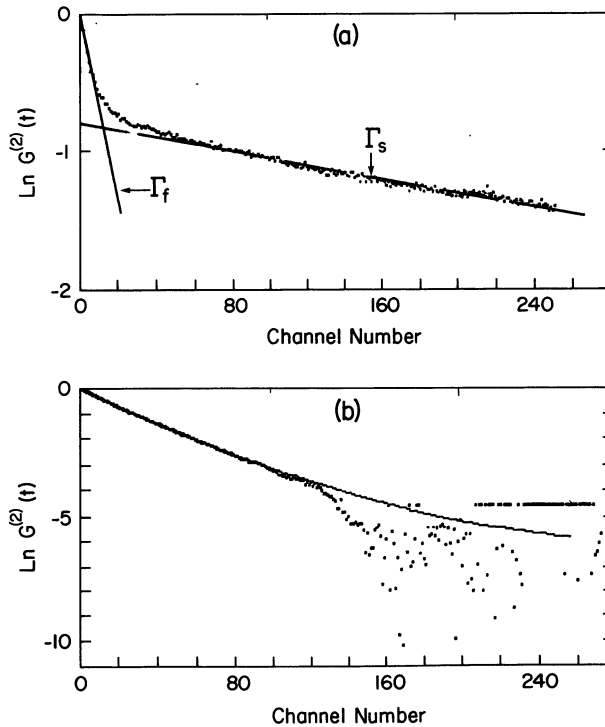


Fig. 2. — Semi-logarithmic plot of the intensity correlation function $G^{(2)}(t)$ vs. channel number. The time t is the product of the channel number and the sample time (s.t.): (a) case of a salt-free solution, polymer concentration $c_P = 0.3$ g/l, s.t. = 80 μ s, $\theta = 15^\circ$; it exhibits two modes; (b) solutions with added sodium chloride: $c_P = 0.3$ g/l, $c_S \approx 0.008$ M, s.t. = 300 μ s, $\theta = 15^\circ$, there is only one mode of fluctuations.

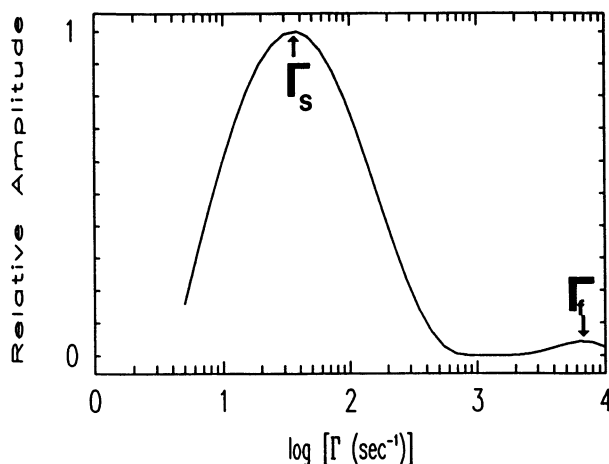


Fig. 3. — Variation of the normalized function $G(\Gamma)$ with $\text{Log } \Gamma$. Two peaks characterize the existence of two separate modes of fluctuations : Γ_f and Γ_s .

ξ_H , S_H), rules out the idea of attributing them to a bimodal macromolecular distribution, since the fast mode is about two orders of magnitude larger than the slow one.

Let us first discuss the origin of the two separate modes. Their existence is a direct consequence of repulsive interactions between neighboring charges along the polymer chain. The high expansion, therefore, imposed to the macromolecules drops the system into the « semi-dilute » case as soon as a small amount of polymer is dissolved into the solution. This is made easier by two factors : the strong polarity of the water molecules and the high molecular weight of the solute macromolecules.

The present set of data should also be discussed in the light of other work. The major features registered for this case : weakness of the intensity and the two mode processes for the fluctuations, have also been observed for the PPV precursor in methanol solutions [29]. Sulfonated polystyrene ionomers with a low degree of sulfonation (4 %-6 %) in DMSO, also showed two decay rates for salt-free solutions, in comparison to neutral polystyrene [17]. Other QELS work undertaken on biological materials (DNA and poly (L-Lysine) for instance) have pointed to the presence of two different relaxation modes accompanied by an important decrease in the scattered intensity when the ionic strength of the solution was brought to very small values [9-13]. Nevertheless, this preliminary agreement involving the relaxation process and the scattered intensity does not screen out some major differences, which come out from a closer analysis of the data. The hydrodynamic correlation length ξ_H , which was measured to be about 12 Å for the present case, needs to be compared to its value in methanol $\xi_H = 17$ Å and also to the one for SPS of reference [17] : $\xi_H = 40$ Å.

The smallness of ξ_H in aqueous solutions when compared to the case of solutions in methanol, could be attributed to the difference in polarity strength of the two solvents. This parameter governs the electrostatic interactions, and therefore the macromolecular expansion. In fact, the dielectric constant ϵ is about 78 (SI) for water ; it is only 32.5 (SI) for methanol. The difference in polarity strength between these two solvents could also play an important role in defining the effective charge density along the polyion backbone, mainly within the prospect of a partial condensation process [29]. In fact, the dipole SCI carried by the PPV precursor monomer is « weak » and its dissociation can be very sensitive to the environment polarity. However, the relatively large value of ξ_H for SPS in DMSO [17] cannot

be only attributed to the solvent polarity strength effect : ϵ (DMSO) = 47 ; it is larger than the value for methanol, but SPS macromolecules carry a lower charge density along their backbones. The combination of these two factors for SPS in DMSO may provide a relatively large value for the hydrodynamic correlation length when compared to the PPV precursor cases. A close investigation of the data, to check an eventual dependence of D_C , D_S on different parameters c_P , c_S , etc., did not provide useful results primarily because of the very weak scattered intensity. This goal is also beyond our present purpose, since c_P is too small to undertake such difficult analysis.

The slow coefficient D_S is often attributed to the center of mass motion. However, such attribution is not obvious for the present case. The amount of polymer dissolved is very small, and using the semi-dilute concepts is not straightforward. Other reasons such as plasma (charges) waves, with large scale fluctuations, could also take place in similar ionic media. More detailed data for this case of salt-free solutions are needed in order to make any useful comparison with theoretical considerations.

b. SOLUTIONS WITH ADDED COUNTERIONS. — We now discuss the effects induced by the presence of a small quantity of conventional electrolyte in the solutions. First, there is a fundamental change in the form of the intensity correlation function $G^{(2)}(t)$ when a small amount of sodium chloride is added to the solution. It shows only one decay rate, Γ (Fig. 2b), of the same order of magnitude as Γ_S for the previous case. We did check that the relation $\Gamma = D_{ef} q^2$ holds for the domain of θ scanned. The existence of only one decay rate for $G^{(2)}(t)$ is indicative of a diffusion process governed by Brownian motion of « isolated » objects in these solutions. The second important point concerns the diffusion coefficient (D_{ef}) thus, deduced as well as R_H . These values are independent of both c_P and c_S for salt concentrations above a certain threshold c_S^* (about 0.002 M) and for the range of c_P scanned (Fig. 4a, b)). Solutions with salt concentrations below c_S^* are also characterized by the appearance of two modes, as previously discussed for salt-free solutions. However, the corresponding decay rates differ from Γ_S and Γ_C (for $c_S \approx 0$) and fluctuate from one solution to another.

This set of results is unusual and different from what has been reported for flexible polyelectrolyte macromolecules. The most striking fact is the absence of dependence of D_{ef} on c_S . In fact, a variation of the mutual diffusion coefficient and also the single chain one $D_{ef}(c_P \rightarrow 0)$ has been recorded for flexible compound : sulfonated polystyrenes with a wide range of charge density have given mutual diffusion coefficients that depend on c_S [18]. A similar behavior has been observed for poly (L-Lysine) solutions [9]. Solutions of DNA and BSA have also showed a complex dependence of D_{ef} ($c_P \neq 0$) on c_S , when the ionic strength is increased. Moreover, the present solute macromolecules showed a different behavior in methanol : a complex variation of D_{ef} with concentration of solute polyions and added salt [29]. Consequently, the increase of the ionic strength of the solution ($c_S > 0.002$ M) seems to induce a sharp and « definite » change in the conformation of the macromolecules in aqueous solutions.

For dilute polymer solutions, an expression accounting for the solute interactions (thermodynamic and hydrodynamic) for the mutual diffusion coefficient reads as [32] :

$$D_{ef} \approx D_T^0 (1 + k_D [\eta] c_P) \quad (10)$$

where D_T^0 is the infinite dilution diffusion coefficient, $[\eta]$ is the intrinsic viscosity coefficient, and k_D depends on the second virial coefficient A_2 and the molecular weight :

$$k_D \approx (2 A_2 M / [\eta]) c_1 - c_2 \quad (11)$$

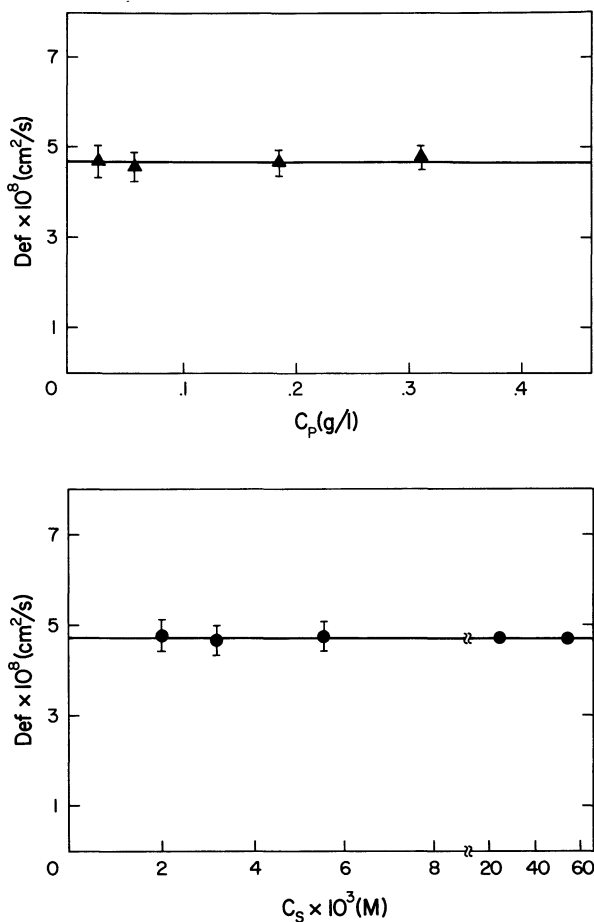


Fig. 4. — (top) Plot of the effective diffusion coefficient D_{ef} vs. polymer concentration c_p for a given salt concentration value $c_s \approx 0.008$ M. (bottom) Plot of the diffusion coefficient D_{ef} v.s. salt concentration c_s for a given polymer concentration $c_p = 0.3$ g/l.

c_1 and c_2 are two constants of the order of 1 [32]. An analysis of the experimental data within the framework of such an expression did provide a good basis to explain the complex variation of D_{ef} with both polymer concentration and ionic strength in methanol [29].

However, this expression does not seem to reflect the type of dependences of D_{ef} on these respective parameters. There may be two explanations that one can think of :

(1) the addition of sodium chloride ions to the solution could have brought the solutions to a θ condition, for c_s large enough. Therefore, the second Virial coefficient is zero and the dependence on c_p will strongly weaken, and could even become negative. However, this suggestion could not explain why the diffusion coefficient D_{ef} does not vary with the ionic strength of the solution. We tried to scan much smaller values of polymer concentrations in order to check an eventual dependence of D_{ef} on c_p . It was not possible to extract any useful data, given the extreme weakness of the scattered intensity. Consequently, it would be safer to ignore the range of extremely small concentrations : $c_p < 0.1$ (g.l) ;

(2) the second attempt is based on entropic consideration and seems more likely to provide an explanation to the present set of data (Fig. 4a, b). Within these considerations, one needs to think of the difference between the two solvents (water and methanol) on a molecular level and from a statistical mechanics point of view. The hydrophobic interactions, purely of entropic nature, are special properties experienced by hydrocarbon compounds in the presence of water molecules. A close analysis, at the molecular level, of the PPV precursor macromolecules shows that they are made of two parts: the side groups (tetra hydrothiophenium chloride) which carry the dipoles SCl, and consequently are very sensitive to polar environment; and the hydrocarbon backbone (phenylene vinylene). The skeleton is very likely to experience hydrophobic interactions when exposed to water molecules. The solvation properties of these chains, in water, is made possible mainly because of the side group dipoles interactions with those of water molecules. Within the framework of this reasoning, the presence of extra counterions screens out the Coulomb repulsive interactions, which were responsible for the polymer chain extension. The screening of the charge-charge repulsion along each backbone, leads the solute molecules to interact with the water molecules as a hydrocarbon chain. Hydrophobic effects could therefore be manifested in a collapse, and very likely association of the macromolecules in the solution. Such phenomenon could explain the important increase of the scattered intensity. It provides isolated aggregates in the medium, which are also very weakly sensitive to the variation of the ionic strength of the environment for $c_S > c_S^*$. More, this process could provide an explanation for the lack of dependence of D_{ef} on c_P , for relatively small polymer concentrations. Within the framework of equation (10) for D_{ef} , the collapse and association processes manifest themselves in the simultaneous effects on both D_T^0 and $k_D[\eta]$. This could induce a cancellation between the increase in solute objects and their mutual interactions within the solution. More, the manifestation of hydrophobic interactions could explain the difference in behavior of PPV precursor macromolecules when dissolved in methanol and in water. This hypothesis (collapse and eventually association of the macromolecules at high enough salt) agrees with what occurs at higher ionic strength: for c_S larger than 0.5 M, a precipitation process of the solute macromolecules takes place [23-26]. Therefore, one can think of the precipitation process as a late state of the collapse-association of the solute macromolecules, when the salt concentration becomes high enough. The precipitation does not occur in methanol for which the solvation of NaCl levels off before any other phenomenon could occur [29]. The lack of dependence of the diffusion coefficient, for very dilute solutions ($c_P \rightarrow 0$) on c_S , was also observed for biological macromolecules such as DNA and BSA [15, 18, 19]. This was primarily attributed to the absence of a conformational change in these naturally rigid macromolecules.

Finally, it would be useful to compare the hydrodynamic size R_H deduced in the present case to the one from methanol solutions at infinite dilution and very high ionic strength [29]:

$$R_H = 550 \text{ \AA} \text{ in water} \quad \text{and} \quad R_H \approx 375 \text{ \AA} \text{ in methanol.}$$

A simple comparison between these two sizes would consolidate the hypothesis of association discussed above. In fact, the value of R_H measured in methanol verifies the relation $R_G/R_H \approx 1.5$ (R_G is the radius of gyration) [29], and could therefore be attributed to a single chain size.

Conclusion

Using QELS technique, we scanned the dynamics of a flexible polyelectrolyte in solution. The solutions experience two different behaviors depending on whether electrolyte (NaCl)

was added to the system or not. For salt-free solutions, the repulsive electrostatic interactions between neighboring charges on the same macromolecule impart to them an extended conformation. This was reflected in the existence of two independent modes for the concentration fluctuations. The addition of counterions induces an « unusual change » in the solution properties. The dynamics are no longer characterized by two modes for the fluctuations. The mutual diffusion coefficient is found to depend on neither the solute nor on the salt concentrations, for the range of values we scanned. This type of behavior is attributed to an eventual manifestation of the hydrophobic interactions, when the ionic strength of the solution is raised sufficiently. To check the validity of such a hypothesis, a small angle neutron scattering experiment could provide an answer. Using the mixing labeling technique, one could have access to the single chain dimension in both cases : very low and high enough ionic strengths. Viscosity measurements could also provide complementary results for the present set of data.

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