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Dynamics of polyelectrolyte solutions by light scattering

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Résumé. — La diffusion quasiélastique de la lumière a été utilisée pour étudier l'évolution du coefficient de diffusion mutuelle en fonction de la concentration en polyélectrolyte et en sel ajouté pour du polystyrène sulfonate de sodium (NaPSS). En régime concentré, sans sel ajouté, deux temps de relaxation sont observés. La valeur du temps de relaxation rapide est en accord avec les résultats obtenus en diffusion des neutrons. L'addition de sel met en évidence une transition des temps de relaxation.

Abstract. — Quasi elastic light scattering was used to investigate the polyelectrolyte and added salt concentrations dependence of the mutual diffusion coefficient of sodium polystyrene sulfonate (NaPSS). Without added salt, two relaxation times are observed in the concentrated regime. The value of the fast component of the effective diffusion coefficient is in agreement with the results of spin echo neutron scattering experiments. The increase of salt concentration results in a splitting of the relaxation times.

In a previous paper [1] it was shown that there is a q dependence of both the scattered intensity and the effective diffusion coefficient of dilute aqueous solution of sodium polystyrene sulfonate (NaPSS). The scattered intensity is characterized by a broad peak for q between 10^{-3} and $3 \times 10^{-3} \text{ \AA}^{-1}$. The q value corresponding to the maximum intensity varies as $C^{1/2}$ for the whole range of concentration (C is the polyelectrolyte concentration). The diffusion coefficient shows a clear minimum around q values where the maximum in the structure factor is observed. For these very low concentrations ($C \sim 10^{-2} \text{ g/l}$ or $0.5 \times 10^{-4} \text{ mono M}$), it was impossible to study in detail the shape of the autocorrelation function so as to find the different decay modes; the experimental time dependence chiefly reflects a mixture of fast and slow relaxation processes. Some qualitative information was given by the q dependence, which indicates a predominance of concentration fluctuations. Generally, the cooperative mode or fast mode relaxation reflects these fluctuations, whereas the slow mode is difficult to characterize (reptation modes of individual chains [2] or diffusion of short structural domains due to the interchain interaction with a large correlation length). In the present paper, we report an investigation of the influence of the polyelectrolyte and added salt concentrations in semi-dilute and concentrated regimes on the effective diffusion coefficient of NaPSS.

We have studied a sample of NaPSS ($M_w \simeq 10^{+5}$) without added salt at very high concentration ($C \simeq 70$ g/l). This concentration corresponds to those investigated by quasielastic neutron scattering [3, 4] where the q -dependent diffusion coefficient increases sharply for $q < q_M$ (q_M is the value of q which induces the maximum of scattered intensity). At $q \sim 1.3 \times 10^{-3} \text{ \AA}^{-1}$, we find two separate relaxation times. Then, a polyelectrolyte concentration dependence of diffusion coefficient at $q \ll q_M$ is measured over a wide range from 0.1 g/l to 70 g/l to determine the respective evolution of the decay modes. A last, the influence of the added salt concentrations on the dynamic properties is reported to show the bizarre splitting between slow and fast relaxation times [5].

1. Materials and methods.

We use NaPSS of molecular weight $M_w = 1 \times 10^5 \text{ g mol}^{-1}$ supplied by Pressure Chemical Co. It is dissolved in water which is very carefully deionized (18 M Ω cm) and filtered through a millipore filter of pore size 0.22 μm . The filtered solution is introduced into light scattering cell. All manipulations are made in an air-cleaned hood (ADS Lamineaire MV 29) so as to eliminate dust particules larger than 0.2 μm . Samples are centrifuged at 5000 rpm for an hour before measurements.

The QLS instruments which has been used in this study and the experimental procedure have been described previously [1, 6]. Autocorrelation functions are analysed by the method of cumulants and are performed in the homodyne mode. Sometimes, the intensity correlation function is clearly the sum of two exponential functions where the average decay rate values $\bar{\Gamma}_i$ are in the ratio of approximately 10^3 or $10^2 : 1$. It is thus necessary to make two experiments on each solution using sampling times differing by a large factor. The sampling time is chosen so that the 64 channels covered 2-4 relaxation times in the observed process. In the short sampling time experiment (0.1-2 μs) the effective fast diffusion coefficient is about 10^{-6} - $10^{-7} \text{ cm}^2/\text{s}$. From autocorrelation functions which are calculated with long channel times (20 μs -100 μs), one obtains a slow effective diffusion coefficient : $D_{\text{eff}}^s \simeq 10^{-8}$ - $10^{-9} \text{ cm}^2/\text{s}$. Generally, the deviation from a single exponential behaviour is large for the low-scattering solutions (with no added salt). The deviation factor μ^2/Γ^2 [6] is calculated as the mean value over the whole time range and leads to a value of 0.3-0.4.

2. Results and discussion.

2.1 EFFECTIVE DIFFUSION COEFFICIENT AT $q \simeq 1.3 \times 10^{-3} \text{ \AA}^{-1}$ FOR NaPSS ($C = 70$ g/l). — Figure 1 shows the q dependence of effective diffusion coefficient measured by spin-echo neutron scattering between $q \simeq 0.05 \text{ \AA}$ and $0.2 \text{ \AA}$ [3, 4]. The data obtained by light scattering are also shown. Two relaxation times are observed : one fast diffusion coefficient $D_{\text{eff}}^f \simeq 30 \times 10^{-7} \text{ cm}^2/\text{s}$ which is consistent with the q dependence obtained from neutron scattering results. It is roughly aligned with the values of the effective diffusion coefficient measured by spin-echo neutron scattering at higher q values. A very sharp decrease is observed but this does not agree with a q^{-2} dependence [3]. A second very slow decay mode is present with a large amplitude of the scattered intensity and the value of the effective diffusion coefficient D_{eff}^s is about $4.8 \times 10^{-9} \text{ cm}^2/\text{s}$. Let us note the very large difference between the values of the diffusion coefficient. The time constants (τ_f and τ_s) are directly proportional to the square of the scattering vector (q^2) and are therefore considered to represent a diffusion process.

The fast mode may correspond to the cooperative diffusion coefficient which reflects the concentration fluctuation due to the polyions and counterions. The slow mode measured at $q \simeq 1.3 \times 10^{-3} \text{ \AA}^{-1}$ is about 1 000 times smaller than the fast relaxation decay. The origin of the slow mode is still unknown [7] but can be correlated to chain reptation mode [2] or to slow concentration fluctuations of large domains (isotropic phase) [8].

Fig. 1. — Effective diffusion coefficient *versus* wave number q for NaPSS ($C \simeq 70$ g/l). (●) Data obtained by neutron quasi elastic scattering (spin-echo spectrometer) (Fig. 5, Ref. [4]). (■) Data obtained by neutron quasi elastic scattering (spin-echo spectrometer) in excess of added salt (Fig. 1, Ref. [3]). (O) Fast relaxation time obtained by quasi elastic light scattering ($q \sim 1.3 \times 10^{-3} \text{ \AA}^{-1}$) $D_{\text{eff}}^f \simeq 30 \times 10^{-7} \text{ cm}^2/\text{s}$. (Δ) Slow relaxation time obtained by quasi elastic light scattering ($q \simeq 2.3 \times 10^{-3} \text{ \AA}^{-1}$) $D_{\text{eff}}^s \simeq 0.05 \times 10^{-7} \text{ cm}^2/\text{s}$. (□) Data obtained in quasi elastic light scattering ($q \simeq 2.3 \times 10^{-3} \text{ \AA}^{-1}$) in excess of salt, $D \simeq 7 \times 10^{-7} \text{ cm}^2/\text{s}$.

2.2 POLYELECTROLYTE CONCENTRATION DEPENDENCE OF EFFECTIVE DIFFUSION COEFFICIENTS. —

Figure 2 shows the dependence of the fast and slow diffusion coefficients (D_{eff}^f , D_{eff}^s) as a function of the polyelectrolyte concentration from 70 g/l to 0.1 g/l in both the semi-dilute $C > C^*$ and concentrated regime $C > C^{**}$ [9, 10] ($C^* \simeq 0.3$ g/l and $C^{**} \sim 8$ g/l). According to the concentration regime, two different behaviours are observed.

— For $C > C^{**}$ which is defined as the concentration where the deformed lattices definitively melt [10], the system is in an « isotropic phase » and the chain is contemplated as an ideal chain of « blobs » [9]. In this concentration range, we observe two relaxation times : the fast relaxation time or D_{eff}^f is roughly C independent and the average value of D_{eff}^f is about $3 \times 10^{-6} \text{ cm}^2/\text{s}$. Neutron spin echo experiments show the same independence of D_{eff}^f with C . Whatever the q range, D_{eff}^f is C independent. In the coupled-mode theory, D_{eff}^f represents the Nernst-Hartley diffusion coefficient, which is independent of the polyelectrolyte concentration. Our experimental results show that the slow mode is decreasing with increasing polyelectrolyte concentration in contradiction with the data of Gruner *et al.* [11] but in agreement with the results of Koene and Mandel [2] obtained with NaPSS ($M_w = 6.5 \times 10^5$ and 12×10^5). The origin of this slow mode is not clear. We have considered the reptation model proposed by Koene and Mandel [2].

The theoretical curves shown in figure 2 are calculated from the reptation model

$$D_{\text{rep}} \sim \frac{2 L_e [(1 - L_e/l)(1 - e^{-l/L_e})]}{\beta \eta l^2}$$

where

L_e is the electrostatic length [10]

l is the contour length

β is Boltzmann's factor

η is the viscosity of the solvent.

$D_{1\text{rep}}$ is obtained according Manning's condensation

$$L_e = (16 \pi a Q C)^{-1},$$

$D_{2\text{rep}}$ is calculated in neglecting the condensation approach

$$L_e = (16 \pi a^2 C)^{-1}$$

a is the average spacing between charges

Q is the Bjerrum length.

Fig. 2. — Logarithmic plot of the effective diffusion coefficient *versus* the polyelectrolyte concentration. $D_{1\text{rep}}$ and $D_{2\text{rep}}$ are deduced from Mandel's model of reptation [2]. $C^{**} \simeq 8$ g/l is the critical concentration between semi-dilute and concentrated regime.

The theoretical curve ($D_{1\text{rep}}$) is in qualitative agreement with the experimental results. However, because the quasi-elastic light scattering method does not allow the individual motion of macromolecules to be observed directly, this reptation model is speculative. A diffusive process resulting from interchain domains having a large correlation length may explain the observed slow relaxation time in agreement with the results obtained with added salt.

— For $C^* < C < C^{**}$ we only observe a slow mode relaxation, and the fast mode can no longer be detected at polyelectrolyte concentrations lower than C^{**} . In this region, D_{eff}^s is C independent and can represent the free diffusion motion of chain. From the classical expression

of Perrin, with $l = 1\,200\text{ \AA}$, one finds $D \simeq 10^{-8}\text{ cm}^2/\text{s}$. One can consider that, in this regime, the different polyions overlap each other, the pseudo-structure is deformed or partially molten. Several conformations have been proposed [9] and the effective diffusion coefficient observed at $C < C^*$ may simply reflect the cooperative motion of some pseudo-structural domains.

2.3 INFLUENCE OF ADDED SALT ON THE EFFECTIVE DIFFUSION COEFFICIENT. — Koene and Mandel have investigated the influence of added salt on NaPSS by quasi elastic light scattering experiments [12]. They found that the prediction of the scaling approach to the cooperative diffusion is well confirmed and they give a very good analysis of the dynamics of aqueous polyelectrolyte-salt solutions.

We have investigated NaPSS solution as a function of the added salt (NaCl and CaCl_2) over a wide range of ionic strengths (from 10^{-4} M to 1 M) and for different polyelectrolyte concentrations.

Figure 3 shows the effect of added salt for $C^{**} > C > C^*$ (polyelectrolyte concentration is about 1 g/l). One finds a precipitous increase of more than an order of magnitude as the salt concentration is increased. Lin *et al.* [5] and K. Schmitz [13] have observed the same bizarre behaviour on poly(L-lysine) which is a cationic polyelectrolyte and they have described these observations as an « extraordinary-ordinary phase transition ».

The slow mode increases with increasing salt concentration (0 – 10^{-3} M NaCl). At 10^{-3} M , the autocorrelation function displays an unusual behaviour and contains both faster and slower components. The scattered intensity increases rapidly and for $c_s > 10^{-3}\text{ M NaCl}$ only a fast relaxation mode is observed. It decreases with increasing added salt concentration, in agreement with the classical behaviour of globular macromolecules in water/salt solution [6]. In excess of salt D_{eff} is about $4 \times 10^{-7}\text{ cm}^2/\text{s}$.

Fig. 3. — Logarithmic plot of effective diffusion coefficient D_{eff} versus added salt concentration (NaCl) at 25°C for $C < C^{**}$. Polyelectrolyte concentration is 1 g/l or $4.8 \times 10^{-3}\text{ mono M}$.

An example of the influence of added salt in the concentrated regime with $C > C^{**}$ is represented in figure 4 (polyelectrolyte concentration is about 40 g/l). The variation of both slow and fast relaxation times is shown and we observe a polyelectrolyte concentration independence of slow

Fig. 4. — Logarithmic plot of effective diffusion coefficient D_{eff} versus added salt concentration NaCl at 25 °C for $C > C^{**}$. Polyelectrolyte concentration is 40 g/l or 0.20 mono M.

mode. Between 5×10^{-2} M and 10^{-1} M (NaCl) the amplitude of scattered intensity due to the slow mode becomes very low and we measure only the fast effective diffusion coefficient, which decreases with the polyelectrolyte concentration.

Whatever the polyelectrolyte concentration, one finds a critical salt concentration to reveal the fast-slow relaxation time splitting. The influence of CaCl_2 on NaPSS is similar, but for a same polyelectrolyte concentration, the « transition » is shifted. For example : with $C = 7$ g/l, $C_s^{\text{NaCl}} = 6 \times 10^{-3}$ M and $C_s^{\text{CaCl}_2} \simeq 1 \times 10^{-3}$ (see Table I).

A general relationship can be proposed to describe this « transition ». Taking into account Manning's theory of the condensation of counterions [14] and the influence of Debye screening due to the added salt, the following expression can be used :

$$\frac{C_p}{\sum_i C_i Z_i^2} \left(\frac{a}{Q} \right) = Z_s$$

C_p is the polyelectrolyte concentration in mono M

$\sum_i C_i Z_i^2$ is the Debye screening due to the added salt (species i , molarity C_i , valency Z_i)

Z_s is the valency of counterion of added salt.

With NaCl and CaCl_2 , the transition appears as :

$$\frac{C_p}{2 C_s} \left(\frac{a}{Q} \right) = 1 \quad \text{or} \quad C_p \simeq 5.8 C_s$$

and

$$\frac{C_p}{6 C_s} \left(\frac{a}{Q} \right) = 2 \quad \text{or} \quad C_p \simeq 34 C_s, \quad \text{respectively.}$$

Figure 5 shows the experimental results obtained on NaPSS solution. A linear relationship is observed between polyelectrolyte and salt concentration at the fast-slow time transition. The experimental data are in good agreement with the proposed relationship (Table I). Two separate

Table I. — *Polyelectrolyte and added salt concentrations involving the slow-fast relaxation time transition.*

C g/l ⁽¹⁾	C_p mono M ⁽²⁾	C_s M ⁽³⁾	$\frac{C_p}{\sum_i C_i Z_i^2} \left(\frac{a}{Q}\right)^{(4)}$	Z_s ⁽⁵⁾
		<u>NaCl</u>	$\frac{C_p}{2 C_s} \left(\frac{a}{Q}\right)^{(4a)}$	1
0.2	10^{-3}	2×10^{-4}	0.90	—
1	4.8×10^{-3}	10^{-3}	0.86	—
5	24×10^{-3}	5×10^{-3}	0.86	—
7	34×10^{-3}	6×10^{-3}	1	—
15	73×10^{-3}	13×10^{-3}	1	—
		<u>CaCl₂</u>	$\frac{C_p}{6 C_s} \left(\frac{a}{Q}\right)^{(4b)}$	2
7	34×10^{-3}	1×10^{-3}	2.02	—

⁽¹⁾ Polyelectrolyte concentration in g/l

⁽²⁾ Polyelectrolyte concentration in mono M or eq/l

⁽³⁾ Added salt concentration in M

⁽⁴⁾ Ratio between free small counter-ions from polyion $\left(C_p / \left(\frac{a}{Q}\right)\right)$ and the part of ionic strength due to added salt $\left(\sum_i C_i Z_i^2\right)$

^(4a) Ratio for NaCl

^(4b) Ratio for CaCl₂

⁽⁵⁾ Z_s is the valency of counter-ions of added salt.

regions I and II characterize the dynamics of charged macromolecules. In I $\left(\frac{C_p}{2 C_s} \left(\frac{a}{Q}\right) > 1\right)$, we observe a peak in the scattered intensity plotted as a function of q . A slow relaxation time is always present whatever the concentration polyelectrolyte regime. For $C > C^{**}$, a fast decay mode which represents a cooperative diffusive process is also observed.

At $\frac{C_p}{2 C_s} \left(\frac{a}{Q}\right) = 1$, the transition appears, the interactive peak disappears and the scattered intensity is strongly increasing. In II $\left(\frac{C_p}{2 C_s} \left(\frac{a}{Q}\right) < 1\right)$, only the fast relaxation time is present and slowly decreases from Nernst-Hartley diffusion process to hydrodynamic diffusion coefficient as the added salt concentration is increased.

Koene and Mandel's study on NaPSS-salt solutions [12] was made in region II. In the semi-dilute region D_{eff} increases with a concentration power law $C_p^{0.75}$ in agreement with the scaling approach and is independent of C_s . At constant C_p the value of D_{eff} decreases with increasing C_s in agreement with our results.

Finally, some comments can be made on the chain conformation in excess of salt. At 40 g/l in excess of salt, D_{eff} is about 6×10^{-7} cm²/s. This value is q independent and corresponds to

Fig. 5. — Logarithmic plot of polyelectrolyte and added salt concentrations which reveals the « slow-fast » time transition. (O) Data for NaPSS/NaCl. (▲) Data obtained from Schurr [5, 17]. (□) Data obtained from Ware [18]. (I) corresponds to $\frac{C_p}{\sum_i C_i Z_i^2} > Z_s$. (a) is the « isotropic » phase ; (b) is the « deformed structural » phase. (II) corresponds to $\frac{C_p}{\sum_i C_i Z_i^2} < Z_s$.

the data obtained without added salt at high q [3]. The coupled mode theory [15] and the generalized Smoluchowski equation approach [16] are in agreement with these results. The strong reduction of D_{eff} upon addition of salt reflects the known increase of structure factor induced by screening. In this case, the extrapolation to $C_p/2 C_s \rightarrow 0$ (low polyelectrolyte concentration in excess of added salt) will be an accurate estimate of $\langle D_H \rangle$ since the electrolyte and interpolyion effects are suppressed ($\langle D_H \rangle$ is the hydrodynamic diffusion coefficient). We obtain $\langle D_H \rangle \simeq 3 \times 10^{-7} \text{ cm}^2/\text{s}$ and R_H (hydrodynamic radius) $\simeq 80 \text{ \AA}$. The dimension R_F of the single chain at infinite dilution must approach the Flory limit and from Odijk's formula [10] we find $R_F = 140 \text{ \AA}$. The gyration radius in the coil conformation is $R_G \sim R_H/0.66 \simeq 120 \text{ \AA}$. The agreement between R_F and R_G in excess of salt is consistent with a coil conformation for a single chain.

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