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On the effect of small ions in the dynamics of polyelectrolyte solutions

L. Belloni and M. Drifford

CEA-IRDI, Département de Physico-Chimie, CEN Saclay, 91191 Gif sur Yvette Cedex, France

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Résumé. — L'effet des petits ions sur la dynamique des solutions de polyélectrolyte est présentée dans le but de compléter une théorie parue précédemment (*J. Physique Lett.* **46** (1985) L-207). Plusieurs formules exprimant le coefficient de diffusion mutuelle des polyions en fonction des concentrations de polyélectrolyte et de sel ajouté sont dégagées. Pour des petits ions ponctuels, ces formules redonnent celles classiquement utilisées pour les systèmes non chargés. Un test quantitatif de ces effets est concrétisé par un bon accord avec des résultats expérimentaux obtenus en diffusion de la lumière sur des solutions de protéine.

Abstract. — The effect of small ions on the dynamics of polyelectrolyte solutions complements a preceding publication (*J. Physique Lett.* **46** (1985) L-207). Expressions for the polyion mutual diffusion coefficient are given as a function of polyelectrolyte and added salt concentrations. For small point-like ions, the classical expressions derived for uncharged systems are deduced. A quantitative illustration of these effects is given : good agreement with light scattering measurements on protein solutions is obtained.

1. Introduction.

The dynamics of micellar and colloidal solutions is often studied through the so-called mutual diffusion coefficient D_m , which can be measured in Quasi-elastic Light Scattering experiments (QELS). It is defined from the first cumulant of the autocorrelation function $I(q, t)$ of the scattered intensity [1] :

$$D_m = - \lim_{q \rightarrow 0} 1/2 q^2 \frac{\partial}{\partial t} \log I(q, t = 0) \quad (1)$$

q is the diffusion vector. The limit $t = 0$ in equation (1) means that the derivative is taken at times t which are long compared to the time between the collisions of the solvent molecules with the particles but short compared to the characteristic times of the Brownian particle motion.

The dynamic behaviour of such solutions is affected by the thermodynamic and hydrodynamic interactions involving the continuous solvent and the polyion and small ion particles.

Many authors in the literature consider these solutions as one-component systems. In this approximation, the small ions are assumed to be point-like and to have an instantaneous diffu-

sion constant. The theoretical treatment of uncharged hard-sphere systems is easily extended to such suspensions and the mutual diffusion constant D_m is expressed in terms of the effective polyion-polyion pair potential, like the DLVO potential [2], through classical relations [3].

On the other hand, the study of polyelectrolyte solutions as multi-component systems is much more complicated. A particular feature of charged suspensions is that one of the characteristic times is a very short relaxation time, known as the plasmon or Debye time τ_D . This time is much smaller than the experimental time in QLS. Therefore, the experimental value of D_m does not correspond to the exact definition (Eq. (1)) but to the following definition,

$$D_m = - \lim_{q \rightarrow 0} \frac{1}{2} q^2 \frac{\partial}{\partial t} \log I(q, \tau)$$

where the experimental time τ is much larger than the Debye time but remains smaller than the diffusional times of the solution. In a recent publication [4], a theoretical treatment of this pseudo mutual diffusion coefficient has been obtained by using the normal mode theory. It was shown that, in the limit of point-like ions, the classical expression for D_m is obtained.

The purpose of this letter consists in deducing from the preceding paper, simpler and more useful expressions for D_m which account for the effect of the non-instantaneous diffusion of small ions on the polyion diffusion. Quantitative illustrations of this effect are given, first, in excess-salt solutions where a virial-type development is available, second, in low concentrated protein solutions. In the latter case, it is shown that the fit of experimental data obtained by QLS is improved in a spectacular way by introducing the finite size of the small ions.

2. Theory.

A polyelectrolyte solution with added salt is considered as a three-component system (polyion 1, counterion 2 and coion 3) of charged hard-spheres. The normal mode theory leads to three dynamical modes; the first one $\Gamma_1 = \tau_D^{-1}$ is the very fast Debye mode, the last two Γ_2 and Γ_3 are diffusional modes, proportional to q^2 . For the experimental time-scale considered here, only the diffusional modes are detected, $\Gamma_1^{-1} \ll \tau \ll \Gamma_2^{-1}, \Gamma_3^{-1}$. The main result of the previous publication [4] gives the relation for the pseudo mutual diffusion coefficient (Eq. (22) of Ref. [4]) :

$$D_m = M_{11}/S_{11} . \quad (2)$$

It is assumed that light is essentially scattered by the large and heavy polyions. $S_{11} = S_{11}(0)$ represents the infinite wavelength limit of the polyion-polyion structure factor $S_{11}(q)$. It is related to the pair distribution function $g_{11}(r)$ by :

$$S_{11} = 1 + \rho_1 \int [g_{11}(r) - 1] dr \quad (3)$$

ρ_i is the number concentration of species i ($i = 1, 2, 3$).

The matrix $\mathbf{M}$, whose (i, i) element appears in equation (2), is [4]

$$\mathbf{M} = \mathbf{H} - 1/\Gamma_1 \mathbf{H} \mathbf{Q}_{DH} \mathbf{H} . \quad (4)$$

The element H_{ij} of the matrix $\mathbf{H}$ represents the hydrodynamic interactions between particles i and j at $q = 0$. It differs from the ideal value $D_i \delta_{ij}$ where $D_i = kT/6 \pi \eta a_i$ is the free-diffusion constant of the species i (sphere of radius a_i). The hydrodynamic term H_j cannot be expressed as simple integrals of the pair distribution functions g_{ij} , except for dilute solutions where the

pair hydrodynamic interactions dominate. In this case,

$$H_{ij} = \left[D_i + kT \sum_k \rho_k \int \hat{\mathbf{q}} \cdot \boldsymbol{\mu}_{iki} \cdot \hat{\mathbf{q}} g_{ik} d\mathbf{r} \right] \delta_{ij} + kT (\rho_i \rho_j)^{1/2} \int \hat{\mathbf{q}} \cdot \boldsymbol{\mu}_{ij} \cdot \hat{\mathbf{q}} g_{ij} d\mathbf{r} \quad (5)$$

$\hat{\mathbf{q}}$ represents the unity vector parallel to $\mathbf{q}$. $\boldsymbol{\mu}_{iki}$ and $\boldsymbol{\mu}_{ij}$ are, respectively, the self and cross pair mobility tensors. Their explicit expression is given by Felderhof [5]. At the Oseen level, $\boldsymbol{\mu}_{iki} = 0$ and $\boldsymbol{\mu}_{ij} = \mathbf{0}$ where $\mathbf{0} = 1/8 \pi \eta r (1 + \hat{\mathbf{r}} \cdot \hat{\mathbf{r}})$ is the Oseen tensor (Eq. (11) of Ref. [4]). The « Debye-Hückel » matrix $\mathbf{Q}_{DH}$ is constituted by the coulombic factors $q_{ij} = 4 \pi L_B Z_i Z_j (\rho_i \rho_j)^{1/2}$. $L_B = e^2 / (4 \pi \epsilon_0 \epsilon kT)$ is the Bjerrum length, Z_i is the charge of species i . The Debye mode Γ_1 is the trace of the matrix $\mathbf{HQ}_{DH}$.

It is important to note that the normal mode theory does not take the so-called memory or relaxation effects into account. These effects are exactly zero for the time-scale $\tau \ll \tau_D$ but have to be explicitied for $\tau_D \ll \tau \ll \Gamma_2^{-1}$, Γ_3^{-1} . We think that the electrofriction described by Schurr [6] is such an effect.

What is the physical meaning of equations (2), (4) ? The first part H_{11} of the term M_{11} gives nothing else than the classical relation for the mutual diffusion constant $D_m = H_{11}/S_{11}$ [1]. The second part shows the influence of small ions on the polyion motion. The diffusions of the different ions are strongly coupled since, at this time-scale $\tau \gg \tau_D$, the local electroneutrality condition must be fulfilled. The contribution of this last part is negative which means that the polyion motion is slowed down by the non-instantaneous ionic diffusion. It disappears in the limit of point-like ions.

If the hydrodynamic interactions are introduced only through the polyion-polyion term, the expression of D_m becomes simpler :

$$M_{11} = D_m S_{11} = H_{11} [1 - H_{11} q_{11} / (H_{11} q_{11} + D_2 q_{22} + D_3 q_{33})]. \quad (6)$$

Quantitative illustrations of the small ions effect are now presented.

3. Results.

3.1 VIRIAL DEVELOPMENT. — In the infinite dilution limit, $\rho_1 \rightarrow 0$, the static and dynamic properties of the solution vary linearly with the polyelectrolyte concentration. The limit $\rho_1 \rightarrow 0$ means that the volume fraction is much smaller than unity and that the counterion concentration of the polyelectrolyte $Z_1 \rho_1$ is much smaller than the added salt concentration ρ_s (excess salt limit). Different virial coefficients can be defined as :

$$\begin{aligned} S_{11}(0) &\sim 1 + k_s \rho_1 \\ H_{11} &\sim D_1 (1 + k_H \rho_1) \\ D_m &\sim D_1 (1 + k_D \rho_1). \end{aligned} \quad (7)$$

The slopes k_s and k_H are given by classical integrals of the infinite dilution value $g_{11}^0(r)$ of the pair distribution function $g_{11}(r)$ [3]. A precise study of equation (5) shows that, even at zero polyelectrolyte concentration, the diffusion coefficient D_1 must be corrected by the self hydrodynamic factor polyion-ion-polyion. In fact, this effect is proportional to the volume fraction of the small ions and hence can be neglected. The problem is to express the k_D slope as a function of the other coefficients.

If the hydrodynamic interactions due to the small ions are neglected, equation (6) can be used and we find a first expression for k_D :

$$k_{D1} = k_H - k_s - (Z_1^2 / 2 \rho_s) (D_1 / D_s) \quad (8)$$

where $D_s = (D_2 + D_3)/2$. For the sake of simplicity, the ions are supposed to be monovalent. The effect of the finite ionic diffusion is clearly shown in equation (8). If this term is suppressed ($D_s \rightarrow \infty$), one obtains the relation for k_D which is classically used for the one-component system [3] :

$$k_{D0} = k_H - k_S. \quad (9)$$

The last term of equation (8) does not correspond to the complete first order in D_1/D_s or a_s/a_1 of the dependence of D_m on the ionic diffusion. Indeed, the polyion-ion hydrodynamic interactions H_{12} and H_{13} , which do not vanish for zero ion radius a_s , are missing in equation (8). The exact first order in D_1/D_s is obtained by calculating the polyion-ion hydrodynamic factors at the Oseen level. Using this approximation, the initial slope k_D of D_m versus ρ_1 becomes, after some simple algebra :

$$k_{D2} = k_H - k_S - \left[D_1 Z_1 - kT\rho_s \int \hat{\mathbf{q}} \cdot \mathbf{0} \cdot \hat{\mathbf{q}} (g_{12}^0 - g_{13}^0) d\mathbf{r} \right]^2 / (2\rho_s D_s D_1) \quad (10)$$

g_{12}^0 and g_{13}^0 are the values of the functions g_{12} and g_{13} , respectively, in the limit $\rho_1 \rightarrow 0$. It seems that the calculation of integral I in equation (10) requires the knowledge of both g_{12}^0 and g_{13}^0 . In fact, the integral can be performed by noting that the difference $g_{12}^0 - g_{13}^0$ arises in the Poisson equation which governs the electrical potential ψ around one polyion ($\varphi = e\psi/kT$) :

$$\begin{aligned} \Delta\varphi &= \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\varphi}{dr} \right) = 0 & r < a_1 \\ &= 4\pi L_B \rho_s (g_{12}^0 - g_{13}^0) & r > a_1. \end{aligned} \quad (11)$$

An integration by part yields for integral I :

$$I = -1/(6\pi\eta L_B \rho_s) \left[\varphi(a_1) + a_1 \frac{d\varphi}{dr}(a_1) \right]. \quad (12)$$

From the Gauss theorem one derives : $d\varphi(a_1)/dr = -Z_1 L_B/a_1^2$. We just need the surface potential $\varphi(a_1)$. A correct value is obtained by the linearized Poisson-Boltzmann model, $\varphi(a_1) = Z_1 L_B/a_1/(1 + \kappa a_1)$. With this value, the slope k_D becomes

$$k_{D2} = k_H - k_S - (Z_1^2/2\rho_s) (D_1/D_s)/(1 + \kappa a_1)^2 \quad (13)$$

$\kappa = (8\pi L_B \rho_s)^{1/2}$ is the Debye screening parameter. Equation (13) differs from equation (8) by the $(1 + \kappa a_1)^2$ factor.

The last development is similar to the calculation of the electrophoretic effect in simple electrolytes.

In order to estimate the magnitude of the last term in equations (8) and (13) relative to the classical term $k_H - k_S$, the slopes k_H and k_S must be calculated. This requires simple numerical integrals of the polyion-polyion distribution function $g_{11}^0(r) = \exp[-\beta v_{11}^{\text{eff}}(r)]$, where $v_{11}^{\text{eff}}(r)$ is the effective pair potential. Numerous expressions of this potential are presented in the literature. A correct and very simple form is [2] :

$$\begin{aligned} \beta v_{11}^{\text{eff}}(r) &= +\infty & r < 2a_1 \\ &= Z_1^2 L_B/(1 + \kappa a_1)^2 \exp[-\kappa(r - 2a_1)]/r & r > 2a_1. \end{aligned} \quad (14)$$

In the Debye-Hückel limit (point charge $a_1 = 0$ and linearization of the exponential $\exp(-\beta v)$), the analytical result is, $k_H = 0$, $k_S = -Z_1^2/2\rho_s$ and

$$k_{D3} = Z_1^2/2\rho_s(1 - D_1/D_s). \quad (15)$$

The relative magnitude of the D_1/D_s term is clear here. This simple expression for the slope k_D , which has been used by many authors [7], is correct for simple electrolytes but fails for polyelectrolytes. The linearization in the Debye-Hückel approximation leads to an overestimate in the value of $k_H - k_s$. Thus, the fit of experimental data with equation (15) always gives values of the polyion charge which are too low.

The differences between the calculated values of k_{D0} , k_{D1} and k_{D2} are illustrated in table I. The physical parameters are $L_B = 7.19 \text{ \AA}$ ($T = 298 \text{ K}$), $a_1 = 25 \text{ \AA}$ ($D_1 \sim 10^{-6} \text{ cm}^2/\text{s}$) and $Z_1 = 30$, which is a correct representation of many aqueous micellar solutions. The values of k_D are given for different salt concentrations, 0.1 M, 0.01 M and 0.001 M.

Expression (15) clearly fails for these highly charged systems. The linearization in the Debye-Hückel treatment is incorrect because of the strong electrostatic repulsion between polyions. The fit of the values k_{D0} with equation (15) is obtained with charges which are listed in table I. These charges are about half the real charge.

The comparison of the slopes k_{D1} and k_{D2} ($D_1/D_s = a_s/a_1 = 1/10$) with the classical expression k_{D0} leads to several conclusions :

First, the k_{D1} and k_{D2} slopes are different, especially at large salinity, arising from the $(1 + \kappa a_1)^2$ factor in equation (13). The suppression of the polyion-ion hydrodynamic interactions overestimates the effect of ionic diffusion. In some cases, the correction $Z_1^2/2 \rho_s D_1/D_s$ is larger than k_{D0} and the slope k_{D1} becomes negative thus giving false results. The correct expression is then equation (13).

The difference of k_{D2} with k_{D0} becomes appreciable with decreasing salt concentration. The relative magnitude of the correction in D_1/D_s compared to $k_H - k_s$ is 23 % at 10^{-3} M salinity although $D_1/D_s = 10\%$. It increases with increasing polyion charge and decreases with increasing size.

This effect is illustrated by experimental results in micellar solutions with low added salt concentration [8] : experimental data of k_D are always smaller than the theoretical k_{D0} but are well fitted with expression (13).

3.2 LOW CONCENTRATED PROTEIN SOLUTIONS. — An interesting test of the present theory is realized by examining the results of Neal, Purich and Cannell [9]. These authors have measured, with fine light scattering experiments, the static structure factor S_{11} and the mutual diffusion coefficient D_m for solutions of charged bovine serum albumin at different macromolecule charges and ionic strengths. The solutions are dilute with regard to the volume fraction ($\sim 0.5\%$ with $a_1 = 35.3 \text{ \AA}$), but not with regard to the electrostatic interactions since the ionic strength is very low. In some cases, the counterions which equilibrate the charge of the polyions are far more numerous than those which come from the added salt. These solutions cannot be considered as excess salt solutions and the linear expressions (7) are not valid : the theoretical values

Table I. — *Theoretical values of the slopes k_s , k_H and k_D (see Eq. (7)), expressed in mol^{-1} , at different added salt concentrations. $a_1 = 25 \text{ \AA}$, $Z_1 = 30$ and $D_1/D_s = 1/10$. $k_{D0} = k_H - k_s$. k_{D1} and k_{D2} are given by equations (8) and (13). The values Z_{fit} represent the erroneous charges which fit the values of k_{D0} with the expression $Z_1^2/2 \rho_s$.*

ρ_s	$-k_s$	$-k_H$	k_{D0}	$Z_1^2/2 \rho_s$	k_{D1}	k_{D2}	Z_{fit}
0.1 M	1 090	535	555	4 500	105	520	10.5
0.01 M	9 230	2 120	7 110	45 000	2 610	5 760	11.9
0.001 M	132 200	12 200	120 000	450 000	75 000	91 700	15.5

of $S = S_{11}$ and H_{11} must be calculated from the distribution functions (Eqs. (3) and (5)), computed with the integral equations HNC [10] or RMSA [11].

Neal *et al.* have found a good adjustment for the structure factor data but a significant deviation for the diffusion coefficient data, especially at low ionic strength. This discrepancy is shown in figure 1 where their measured and calculated values of SD_m/D^0 are plotted *versus* S^{-1} (Fig. 8 of Ref. [9]). Their theoretical curve corresponds to $SD_m/D^0 = H_{11}/D^0$. Since the volume fraction is negligible, the misfit does not result from the fact that the hydrodynamic interactions are included to first order in the concentration. Agreement is obtained by taking account of the non-instantaneous diffusion of ions, namely by using equation (6) (in such solutions, the polyion hydrodynamic interactions can be neglected since $\kappa a_1 \ll 1$). With $D_2 = D_3 = D_s$, the correct expression is then

$$SD_m/D^0 = H_{11}/D^0 [1 - H_{11} Z_1 \rho_1 / (H_{11} Z_1 \rho_1 + 2 ID_s)] \quad (16)$$

$I = \rho_s + Z_1 \rho_1/2$ is the ionic strength.

The theoretical curve given by equation (16) can be obtained, in a very simple manner, from the original curve of Neal *et al.* This curve is plotted on the same figure 1, for two values of the ionic radius a_s , 1.5 Å and 2 Å. As was noted by Neal *et al.* [9], different solutions which lead to identical values of S also lead to similar values of D_m . It is clear that the theoretical diffusion coefficients are reduced, due to the nonzero size of small ions, and tend to the experimental data. The best agreement is obtained with $a_s = 1.5$ Å, which is a reasonable value ($D_s \sim 14 \times 10^{-6} \text{ cm}^2/\text{s} \sim D_{\text{Na}^+}$).

In the absence of salt (the linear coefficients k_s and k_H diverge), the interactions through S^{-1} are maximum and the mutual diffusion coefficient tends to the Nernst-Hartley value, $SD_m = H_{11} D_2 / (H_{11} Z_1 + D_2)$.

4. Conclusion.

Simple expressions for the ionic diffusion effect in the dynamics of polyelectrolyte solutions have been given. The relative magnitude of this correction was shown to be appreciable at low salinity.

Fig. 1. — Experimental and theoretical values for the quantity SD_m/D^0 vs. S^{-1} . S represents the long wavelength limit of the polyion-polyion structure factor, $S_{11}(0)$. D_m is the mutual diffusion coefficient, D^0 its value in absence of interaction. The symbols represent the experimental data of Ref. [9]. The classical theory is shown as a solid line. The noninstantaneous diffusion of small ions is introduced *via* equation (16), with an ionic radius $a_s = 1.5$ Å (---) and $a_s = 2$ Å (—.—).

A good improvement for the fit of experimental results has been obtained. In view to get a more precise picture of the dynamics of charged suspensions, the relaxation of the small ions around the polyions will have to be introduced.

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