



About the correlation between the mobility of a polyion and that of its counterions

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ABSTRACT

In this paper, we propose a new approach in order to interpret the variation of the conductivity of the PSS polyion with the nature and the concentration of the alkaline counter-ions Li^+ , Na^+ and K^+ , and the hydrophobic cations Et_4N^+ and Bu_4N^+ . This approach is based on a recent model in which the stretched polyion is represented by a chain of successive charged spheres, partially condensed by the counter-ions. We have found that the moderate variation of the hydrodynamic friction on the polyion with the size R_M of condensed counter-ions, cannot completely explain the *important* decrease (of about 35% from K^+ to Bu_4N^+) of the conductivity ($\lambda_{\text{PSS},M}$) of the PSS polyion with the nature of the counter-ions. Consequently, we have proposed a supplementary explanation by taking into account of the translational dielectric friction on the moving polyion. Formal analysis of this friction shows that it is very sensitive to the local structure of water surrounding the polyions. As this local structure depends in its turn, on the nature of the condensed counter-ions; we suggested that this specific sensitivity could explain the high dependence of the mobility of the polyion with the nature of its counter-ions.

Keywords

Conductibility; Ionic condensation; Polystyrene sulphonate; Ionic friction; Dielectric friction; Hydrophobic.

Academic Discipline

Physical chemistry.

SUBJECT CLASSIFICATION

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TYPE (METHOD/APPROACH)

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1. INTRODUCTION

Contrary to the case of the simple electrolytes, the conductivity of poly electrolytes does not obey to a universal linear limiting law relating their equivalent conductivity at high dilution to the square root of ionic strength: $I^{1/2}$. Consequently, there is no currently available satisfactory theory describing the dynamic behavior of dilute flexible polyelectrolytes in aqueous solution despite some interesting progress toward this objective [1-10]. This difficulty arises from the complex interdependence between polyion conformation, the processes of condensation of counter-ions M^+ , the ionic screening effect and frictional effects.

In a series of previous papers [11-13], H. Vink proposed a semi-empirical approach for the interpretation of the conductivity of some polyelectrolytes, in order to: a) verify the Manning's theory [3, 8] and: b) to study the dependence of the conductivity of some polyions with the nature of their counter-ions. The main results of these studies concerning dilute MPSS polyelectrolyte solutions are:

- The degree of condensation $(1 - \alpha)$ of counter-ions is practically independent as well as of the concentration and of the nature of studied counter-ions Li^+ , Na^+ and K^+ , and that its value (0.65) is very close to that predicted by the theory of Manning. However, for organic counter-ions (Et_4N^+ and Bu_4N^+), α is in general slightly lower than that of the Manning value $\alpha^{Manning}$.
- The ionic friction coefficient on the polyion (β_{ir}) can be assumed to be equal to that predicted by the Manning's theory.
- The experimental conductivity $\lambda_{P,M}$ of the PSS polyion depends *strongly* on the *nature* of the counter-ion M^+ in a range of concentration between $5 \cdot 10^{-4} M$ and $3.5 \cdot 10^{-3} M$. Indeed, by combining the experimental equivalent conductivities Λ_{MP}^{exp} with their corresponding experimental "transference numbers", $T_{P,M}$, the author has been able to extract for each type of counter-ions and for a given concentration, the conductivity $\lambda_{P,M}$ of the PSS polyion and he has found that $\lambda_{P,M}$ increases with the mobility of the counter-ions in accordance with the following order: $M^+ \equiv H^+, Li^+, Na^+, K^+, Et_4N^+$ and Bu_4N^+ .

However, this last result is qualitatively and quantitatively in complete contradiction with the Manning's theory for which both the degree of condensation $(1 - \alpha)$ and the conductivity $\lambda_{P,M}$ of the PSS polyion are independent on the nature of counter-ions.

The explanation suggested by the author is that the contribution of the condensed counter-ions to the hydrodynamic friction of the polyion increases with their size.

In fact, as polyanions and positive *free* counter-ions move along opposed directions, electrostatic coupling gives therefore place to a process of *braking* rather than to a mutual entrainment. Consequently, $\lambda_{P,M}$ will rather *decrease* with the mobility of the counter-ions (friction effect). In contrast the *condensed* counter-ions are retained by the polyion and the ensemble forms a stable entity without internal frictional coupling resulting from the difference between motilities.

The present work proposes another approach in order to obtain an adequate analytical expression describing correctly the variation of the global conductivity of the MPSS polyelectrolyte with the nature and the concentration of the counter-ions. This new approach is based on a recent model in which the stretched polyion is represented by a chain of successive charged spheres, partially condensed by the counter-ions, and without introduction of specific parameters other than the structural parameters of the polyion, the valence and the effective radius of the counter-ion. Such approach will make it possible to check if the introduction of these only parameters will allow or not to explain the possible dependence of the conductivity of the polyion with nature of the counter-ions.

2. THEORETICAL MODEL OF MANNING

According to the Manning's conductance theory of a salt-free polyelectrolyte solution MP, the conductivity $\lambda_P^{Manning}$ of the corresponding polyion P of L_S structural length and Z_{se} structural charge, is independent on the *nature* of the counter-ion M and varies with its total concentration C_M° ($mol.l^{-1}$) as follows [3, 4]:

$$\lambda_P^{Manning} = -\alpha^{Manning} (Fe/3\pi\eta b_S) \text{Ln}[\chi_D b_S] (1 + \beta_{ir}^{Manning})^{-1} \quad (1)$$

$\lambda_P^{Manning}$ expresses the different friction effects undergone by the polyion i.e.: the hydrodynamic effect, the electrophoretic effect and the ionic relaxation effect via the viscosity η of the solvent ($\eta = 0.8903 \cdot 10^{-2}$ poises for water at 25 °C), the screen parameter χ_D and the ionic friction coefficient $\beta_{ir}^{Manning}$. F is the Faraday so that: $Fe/6\pi = 0.82$. On the other hand, $\lambda_P^{Manning}$ is proportional to the apparent charge of the polyion and therefore to the degree of dissociation $\alpha^{Manning}$ of the counter-ions which is in this case, independent on the *concentration* and on the *nature* of the counter-ions:

$$\alpha^{Manning} = b_S / |Z_M| L_B \quad (2)$$



$b_S = L_S/|Z_S|$, is the distance of separation between two successive ionizable groups, Z_M is the valence of the counter-ion and $L_B = e^2/(\epsilon_0 k_B T)$ is the Bjerrum length, where k_B is the Boltzmann constant and ϵ_0 is the permittivity of the solvent.

$\beta_{ir}^{\text{Manning}}$ is the Manning ionic friction coefficient on the polyion due to the counter-ions which is also independent on the concentration and on the *nature* of the counter-ion [3]:

$$\beta_{ir}^{\text{Manning}} = 0.13 \quad (3)$$

The screen parameter of Debye χ_D is given by:

$$\chi_D^2 = 4\pi 10^{-27} N_A L_B [\alpha^{\text{Manning}} Z_M^2 C_M^{\circ}] \quad (4)$$

N_A is the Avogadro number. For water at 25 °C: $L_B = 7.156 \text{ \AA}$ and C_M° (mol.l⁻¹) is the total concentration of counter-ions. The practical expression of χ_D (in \AA^{-1}) is:

$$\chi_D = 8.7 \cdot 10^{-2} (b_S C_M^{\circ})^{1/2} \quad (5)$$

Note that χ_D^{-1} measure the cylindrical mean radius of the ionic atmosphere around the polyion assumed to be an infinite thread of apparent charge: $Z_{ap} e = (\alpha^{\text{Manning}} Z_S e)$. Combination of (Eq.1, Eq. 2, Eq. 3 and Eq. 5) leads to the following practical expression of $\lambda_P^{\text{Manning}}$ (in $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$):

$$\lambda_P^{\text{Manning}} = -22.78 \text{Ln}[8.7 \cdot 10^{-2} (b_S C_M^{\circ})^{1/2} b_S] \quad (6)$$

It is therefore clear that $\lambda_P^{\text{Manning}}$ is independent of the nature of the counter-ion.

In the other hand, the expression of the ionic conductivity λ_M of the counter-ions M can be decomposed as follows:

$$\lambda_M = (\lambda_M^{\circ} - |\Delta\lambda_M^{\text{el}}|)(1 + \beta_{ir}^{\text{Manning}})^{-1} \quad (7)$$

λ_M° is the ionic equivalent conductivity of the counter-ion at infinite dilution which expresses both the hydrodynamic friction due to the viscosity η of the solvent (Stokes [14]), and the dielectric friction effect [15] caused by the polarization of solvent molecules by the charge $Z_M e$ of the moving counter-ion.

$|\Delta\lambda_M^{\text{el}}|$ measures the electrophoretic effect undergone by the counter-ion. The general expression of $|\Delta\lambda_M^{\text{el}}|$ is according to the Debye-Onsager-Fuoss theory [14] given by:

$$|\Delta\lambda_M^{\text{el}}| = (|Z_M| F e / 6\pi\eta d_M) \quad ; \quad d_M = R_M + (\chi_D)^{-1} \quad (8)$$

R_M is the effective radius of the counter-ion "M" and d_M is the radius of its ionic atmosphere, and χ_D is its corresponding Debye screen parameter. The final expression is therefore:

$$|\Delta\lambda_M^{\text{el}}| = (82|Z_M| / 0.8903) \{ (8.7 \cdot 10^{-2} (b_S C_M^{\circ})^{1/2}) / [1 + 8.7 \cdot 10^{-2} (b_S C_M^{\circ})^{1/2} R_M] \} \quad (9)$$

Now, the Manning expression of the conductivity $\Lambda_{MP}^{\text{Manning}}$ of the polyelectrolyte MP is:

$$\Lambda_{MP}^{\text{Manning}} = \alpha^{\text{Manning}} [\lambda_P^{\text{Manning}} + \lambda_M] \quad (10)$$

Combination of (Eq.2, Eq.3, Eq.6, Eq.7, Eq.9 and Eq.10) leads to the following practical expression of $\Lambda_{MP}^{\text{Manning}}$ (in $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$):



$$\Lambda_{MP}^{Manning} = (b_s / 8.08) \{ \lambda^{\circ}_M - 25.74 \ln [0.087 (b_s C^{\circ}_M)^{1/2} b_s] - 8.01 (b_s C^{\circ}_M)^{1/2} / [1 + 0.087 (b_s C^{\circ}_M)^{1/2} R_M] \} \quad (11)$$

Tables 1a, 1b and Figures 1a, 1b give the variations with the total ionic concentration C°_M of the Manning conductivity $\Lambda_{MP}^{Manning}$ and of the experimental equivalent conductivity Λ_{MP} of a polyelectrolyte MP, corresponding to the following polyelectrolytes (Polystyrene Sulphonates): KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C. Note that the PSS polyanion is characterized by the structural parameters: $L_S = 7250 \text{ \AA}$, $Z_S = -2900$ and therefore $b_s = 2.5 \text{ \AA}$ and $\alpha^{Manning} = 0.35$. We can conclude from these comparisons that conductibilities calculated from Manning's approach are larger than the experimental equivalent conductivity Λ_{MP} .

Table 1a. Variation with the counter-ion concentration C°_M of the Manning conductibilities $\Lambda_{MP}^{Manning}$ and the experimental equivalent conductivity Λ_{MP} of a polyelectrolyte MP, of different polyelectrolytes (Polystyrene Sulphonate MPSS): KPSS, NaPSS and LiPSS in water at 25 °C.

C°_M mol.l ⁻¹	$\Lambda_{KPSS}^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹	Λ_{KPSS} cm ² Ω ⁻¹ equiv ⁻¹	$\Lambda_{NaPSS}^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹	Λ_{NaPSS} cm ² Ω ⁻¹ equiv ⁻¹	$\Lambda_{LiPSS}^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹	Λ_{LiPSS} cm ² Ω ⁻¹ equiv ⁻¹
5 10 ⁻⁴	61.489	44.585	54.242	35.734	50.711	31.879
1 10 ⁻³	58.691	44.210	51.443	35.586	47.912	31.777
1.5 10 ⁻³	57.047	43.921	49.799	35.462	46.269	31.675
2 10 ⁻³	55.877	43.718	48.629	35.364	45.099	31.573
2.5 10 ⁻³	54.968	43.601	47.720	35.290	44.190	31.471
3 10 ⁻³	54.223	43.570	46.975	35.241	43.446	31.370
3.5 10 ⁻³	53.592	43.624	46.344	35.2175	42.815	31.268

Table 1b. Variation with the counter-ion concentration C°_M of the Manning conductibilities $\Lambda_{MP}^{Manning}$ and the experimental equivalent conductivity Λ_{MP} of a polyelectrolyte MP, of different Polystyrene Sulphonate MPSS: Et₄NPSS and Bu₄NPSS in water at 25 °C.

C°_M mol.l ⁻¹	$\Lambda_{Et4NPSS}^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹	$\Lambda_{Et4NPSS}$ cm ² Ω ⁻¹ equiv ⁻¹	$\Lambda_{Bu4NPSS}^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹	$\Lambda_{Bu4NPSS}$ cm ² Ω ⁻¹ equiv ⁻¹
5 10 ⁻⁴	48.853	24.942	44.764	18.100
1 10 ⁻³	46.054	24.525	41.966	17.608
1.5 10 ⁻³	44.411	24.187	40.323	17.202
2 10 ⁻³	43.242	23.927	39.154	16.882
2.5 10 ⁻³	42.332	23.746	38.245	16.646
3 10 ⁻³	41.588	23.643	37.501	16.496
3.5 10 ⁻³	40.957	23.618	36.871	16.432

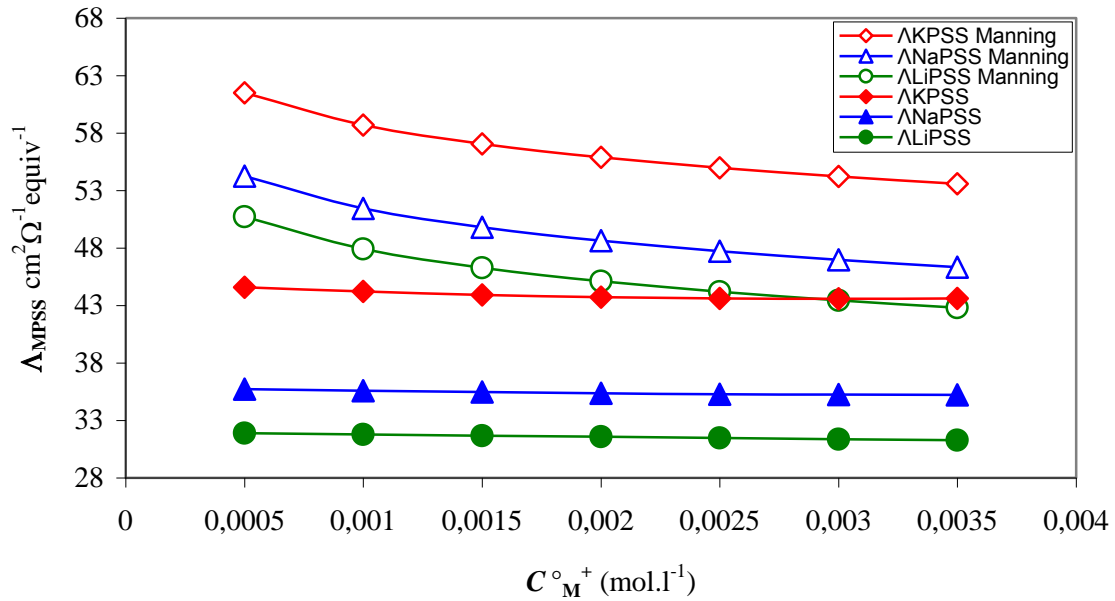


Figure 1a. Comparison for different C_M^+ of: the Manning conductivity $\Lambda_{KPSS}^{Manning}$, $\Lambda_{NaPSS}^{Manning}$, $\Lambda_{LiPSS}^{Manning}$, the experimental conductivity Λ_{KPSS} , Λ_{NaPSS} and Λ_{LiPSS} , for different Polystyrene Sulphonate MPSS: KPSS, NaPSS and LiPSS in water at 25 °C.

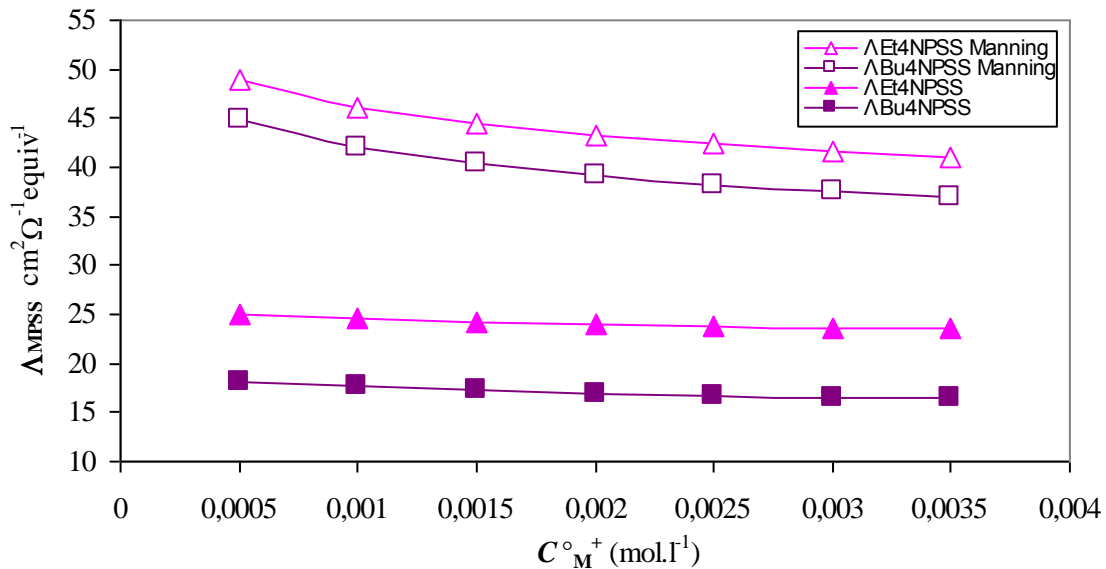


Figure 1b. Comparison for different C_M^+ of: the Manning conductivity $\Lambda_{Et4NPSS}^{Manning}$, $\Lambda_{Bu4NPSS}^{Manning}$, the experimental conductivity $\Lambda_{Et4NPSS}$, $\Lambda_{Bu4NPSS}$ of Et₄NPSS and Bu₄NPSS in water at 25 °C.

3. VINK'S APPROACH

3.1 Principle of Experimental determination of α_M and $\lambda_{PSS,M}$

According to Vink's approach [11-13], the experimental equivalent conductivity Λ_{MP} of a polyelectrolyte MP can be written empirically as following:

$$\Lambda_{MP} \equiv \alpha_M[\lambda_M + \lambda_{P,M}] \approx (1 - \beta_{irP,M})\alpha_M[\lambda'_M + \lambda'_{P,M}] \quad (12)$$



Eq. 12 relates Λ_{MP} to four physical quantities: $\beta_{irP,M}$, α_M , λ'_M and $\lambda'_{P,M}$. As previously, the factor $(1 - \beta_{irP,M})$ represents the interionic friction due to the ionic relaxation effect. It is important to note that from irreversible thermodynamics considerations and for a salt-free polyelectrolyte, the friction coefficient $\beta_{irP,M}$ is the same for polyions and counter-ions [6, 11-13, 16]. α_M is the degree of dissociation of the polyelectrolyte which determines the effective charge $Z_{ap}e$ of the polyion so that:

$$Z_{ap}e = \alpha_M Z_S e \quad (13)$$

Z_S is the stoichiometric charge number of the polyion.

Note that λ'_M and $\lambda'_{P,M}$ are different from respectively the equivalent conductivity of the free counter-ions (λ_M) and from the equivalent conductivity of the polyion ($\lambda_{P,M}$).

All these quantities generally depend on the concentration of the polyelectrolyte and on the nature of the counter-ions. This last dependence is indicated by the index M. The experimental determination of $\beta_{irP,M}$, α_M , λ'_M and $\lambda'_{P,M}$ needs in addition to Eq.12 of three other relations.

The second relation is obtained from the net charge transported by the polyion which is measured by its electric transport number $t_{P,M}$:

$$t_{P,M} = \lambda_{P,M} / (\lambda_{P,M} + \lambda_M) = \lambda'_{P,M} / (\lambda'_{P,M} + \lambda'_M) \quad (14)$$

Where the dependence of $t_{P,M}$ with the nature of the counter-ion is indicated by the index M. However, in solutions with ionic association only the corresponding ionic constituent transport number $T_{P,M}$ is experimentally determinable [12]:

$$T_{P,M} = t_{P,M} / \alpha_M \quad (15)$$

Tables 2a and 2b, give the variation of $T_{P,M}$ and Λ_{MP} with the concentration for different types of counter-ions.

From equations (Eq.14 and Eq.15) we obtain another form of Eq.14:

$$\lambda_{P,M} = T_{P,M} \Lambda_{MP} \quad (16)$$

From Eq.16, $\lambda_{P,M}$ appears as well as a pure experimental quantity because it is related to the experimental values: $T_{P,M}$ and Λ_{MP} .

The third relation is obtained by neglecting the electrophoretic friction undergone by the counter-ions M, for dilute solutions, so that:

$$\lambda'_M \approx \lambda^\circ_M \quad (17)$$

λ°_M is equal to the ionic conductivity of M at infinite dilution.

According to Vink's approach, the fourth relation is obtained by assuming Manning's model for the ionic friction coefficient β_{ir} , so that [13]:

$$(1 - \beta_{irP,M}) = (1 - \beta_{ir}^{\text{Manning}}) = 0.87 \quad (18)$$

It means that β_{ir} is independent on the nature and on the concentration of counter-ions. Logically, in turn, if Eq. 18 is valid, then also: $\alpha_M = \alpha^{\text{Manning}} = b_S / |Z_M|_{LB} = 0.35$. (Or at least $\alpha_M \approx \text{Cste}$: Manning's regime [6-7, 17]). It is possible to test this assumption by calculating α_M after combination of Eqs. (12, 15, 17):

$$\alpha_M \approx \Lambda_{MP} / [(1 - \beta_{ir})\lambda^\circ_M + T_{P,M} \Lambda_{MP}] \quad (19)$$



Table 3 gives for different types of counter-ions the variation of their corresponding α_M with the counter-ion concentration according to Eq. 19, using $(1-\beta_{ir}) = 0.87$, and the experimental values of $T_{P,M}$ and Λ_{MP} given in tables 2a and 2b. It shows that for all ions, α_M increases slowly with the concentration of about 3% in the concentration range between $5 \cdot 10^{-4}$ M and $3.5 \cdot 10^{-3}$ M. On the other hand, α_M values are practically the same for Na^+ and K^+ with a mean value of about 0.35 (i.e. equal to the Manning's value). However, α_M values of Li^+ are larger of about 4.5%. In contrast, α_M values for organic counter-ions Et_4N^+ and Bu_4N^+ are lower (of about respectively 10% and 11.5%). We can conclude that Manning's assumption based on electrostatic condensation seems valid for alkaline ions, but in the case of organic counter-ions, the condensation effect is enhanced by the *hydrophobic* attraction between polyions and organic cations.

Moreover, in order to justify his assumption expressed by Eq. 18, Vink proposed a new method based on the following equation obtained after rearranging Eq. 19:

$$T_{P,M} = (1/\alpha_M) - (1-\beta_{ir}) [\lambda^{\circ}_M / \Lambda_{MP}] \tag{20}$$

Indeed, *if* (in accordance with Manning's theory), both α_M and $(1-\beta_{ir})$ are *independent* on the counter-ion species, we get $(1-\beta_{ir})$ as the slope of the line obtained when $T_{P,M}$ is plotted against $(\lambda^{\circ}_M / \Lambda_{MP})$ (calculated for the different counter-ions; see tables 2a and 2b). However, calculations according to Eqs. (18 and 19), show that for a given concentration $C_M^{\circ+}$, the α_M vary slightly with the nature of the counter-ions. Therefore, we can replace α_M in Eq. (20), by its means value $\langle \alpha_M \rangle$ given in table 3, so that:

$$\langle \alpha_M \rangle^{-1} - T_{P,M} = (1-\beta_{ir}) [\lambda^{\circ}_M / \Lambda_{MP}] \tag{21}$$

Note that this method is valid even if $\langle \alpha_M \rangle$ depends on the counter-ion concentration.

Tables 2a and 2b give the experimental variations with the counter-ion concentration $C_M^{\circ+}$ of Λ_{MP} , $T_{P,M}$ and $(\lambda^{\circ}_M / \Lambda_{MP})$ in the case of different polyelectrolytes (Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et_4NPSS and Bu_4NPSS), in water at 25 °C. All these data allow the calculation for each polyelectrolyte and for different concentrations ($C_M^{\circ+} = 110^{-3}$ M, 210^{-3} M, 310^{-3} M), of its corresponding dissociation coefficient α_M . On the other hand, figure 2 shows that for the three concentrations ($C_M^{\circ+} = 110^{-3}$ M, 210^{-3} M, 310^{-3} M, with respectively: $\langle \alpha_M \rangle = 0.328$, 0.342 and 0.35), the three curves giving the variation of $(\langle \alpha_M \rangle^{-1} - T_{P,M})$ with $(\lambda^{\circ}_M / \Lambda_{MP})$, are practically superimposed on only *one* line passing by the origin, and having a slope $(1-\beta_{ir})$, practically independent on the concentration with a mean value of about (0.87) i.e. equal to that predicted by Eq. 18 and by Manning's theory.

Table 2a. Variation with the counter-ion concentration $C_M^{\circ+}$ of: the experimental conductivity Λ_{MPSS} , the experimental transport number $T_{P,M}^{MPSS}$ and $(\lambda^{\circ}_M / \Lambda_{MPSS})$ of different Polystyrene Sulphonate MPSS: KPSS, NaPSS and LiPSS in water at 25 °C.

$C_M^{\circ+}$ mol.l ⁻¹	Λ_{KPSS} cm ² Ω ⁻¹ equiv ⁻¹	$T_{P,M}^{KPSS}$	$\lambda^{\circ}_{K^+} / \Lambda_{KPSS}$ ($\lambda^{\circ}_{K^+} = 73.5$)	Λ_{NaPSS} cm ² Ω ⁻¹ equiv ⁻¹	$T_{P,M}^{NaPSS}$	$\lambda^{\circ}_{Na^+} / \Lambda_{NaPSS}$ ($\lambda^{\circ}_{Na^+} = 50.1$)	Λ_{LiPSS} cm ² Ω ⁻¹ equiv ⁻¹	$T_{P,M}^{LiPSS}$	$\lambda^{\circ}_{Li^+} / \Lambda_{LiPSS}$ ($\lambda^{\circ}_{Li^+} = 38.7$)
$5 \cdot 10^{-4}$	44.585	1.482	1.6485	35.734	1.885	1.4020	31.879	1.914	1.2139
$1 \cdot 10^{-3}$	44.210	1.439	1.6625	35.586	1.772	1.4078	31.777	1.805	1.2178
$1.5 \cdot 10^{-3}$	43.921	1.399	1.6734	35.462	1.679	1.4127	31.675	1.714	1.2219
$2 \cdot 10^{-3}$	43.718	1.361	1.6812	35.364	1.606	1.4167	31.573	1.641	1.2257
$2.5 \cdot 10^{-3}$	43.601	1.325	1.6857	35.290	1.554	1.4196	31.471	1.588	1.2297
$3 \cdot 10^{-3}$	43.570	1.291	1.6870	35.241	1.522	1.4216	31.370	1.552	1.2336
$3.5 \cdot 10^{-3}$	43.624	1.260	1.6848	35.2175	1.510	1.4225	31.268	1.536	1.2377



Table 2b. Variation with the counter-ion concentration C_M^+ of: the experimental conductivity Λ_{MPSS} , the experimental transport number $T_{P,M}^{MPSS}$ and $(\lambda_M^\circ/\Lambda_{MPSS})$ of Et₄NPSS and Bu₄NPSS in water at 25 °C.

C_M^+ mol.l ⁻¹	Λ_{Et_4NPSS} cm ² Ω ⁻¹ equiv ⁻¹	$T_{P,M}^{Et_4NPSS}$	$\lambda_{Et_4N}^\circ/\Lambda_{Et_4NPSS}$ ($\lambda_{Et_4N}^\circ = 32.7$)	Λ_{Bu_4NPSS} cm ² Ω ⁻¹ equiv ⁻¹	$T_{P,M}^{Bu_4NPSS}$	$\lambda_{Bu_4N}^\circ/\Lambda_{Bu_4NPSS}$ ($\lambda_{Et_4N}^\circ = 19.5$)
5 10 ⁻⁴	24.942	2.122	1.3110	18.100	2.513	1.0773
1 10 ⁻³	24.525	2.056	1.3333	17.608	2.373	1.1073
1.5 10 ⁻³	24.187	1.996	1.3520	17.202	2.264	1.1337
2 10 ⁻³	23.927	1.942	1.3666	16.882	2.187	1.1552
2.5 10 ⁻³	23.746	1.895	1.3771	16.646	2.141	1.1712
3 10 ⁻³	23.643	1.854	1.3831	16.496	2.125	1.1818
3.5 10 ⁻³	23.618	1.819	1.3845	16.432	2.141	1.1868

Table 3. Variation with the counter-ion concentration C_M^+ of the degree of dissociation α_M of different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C. ($\langle \alpha_M \rangle$ is the average degree of dissociation for each concentration).

C_M^+ mol.l ⁻¹	α_K	α_{Na}	α_{Li}	α_{Et_4N}	α_{Bu_4N}	$\langle \alpha_M \rangle$
5 10 ⁻⁴	0.343	0.322	0.336	0.306	0.290	0.319
1 10 ⁻³	0.346	0.334	0.349	0.311	0.299	0.328
1.5 10 ⁻³	0.350	0.344	0.360	0.315	0.307	0.335
2 10 ⁻³	0.354	0.353	0.369	0.319	0.313	0.342
2.5 10 ⁻³	0.358	0.358	0.376	0.323	0.316	0.346
3 10 ⁻³	0.362	0.362	0.381	0.327	0.317	0.350
3.5 10 ⁻³	0.367	0.364	0.383	0.331	0.315	0.352

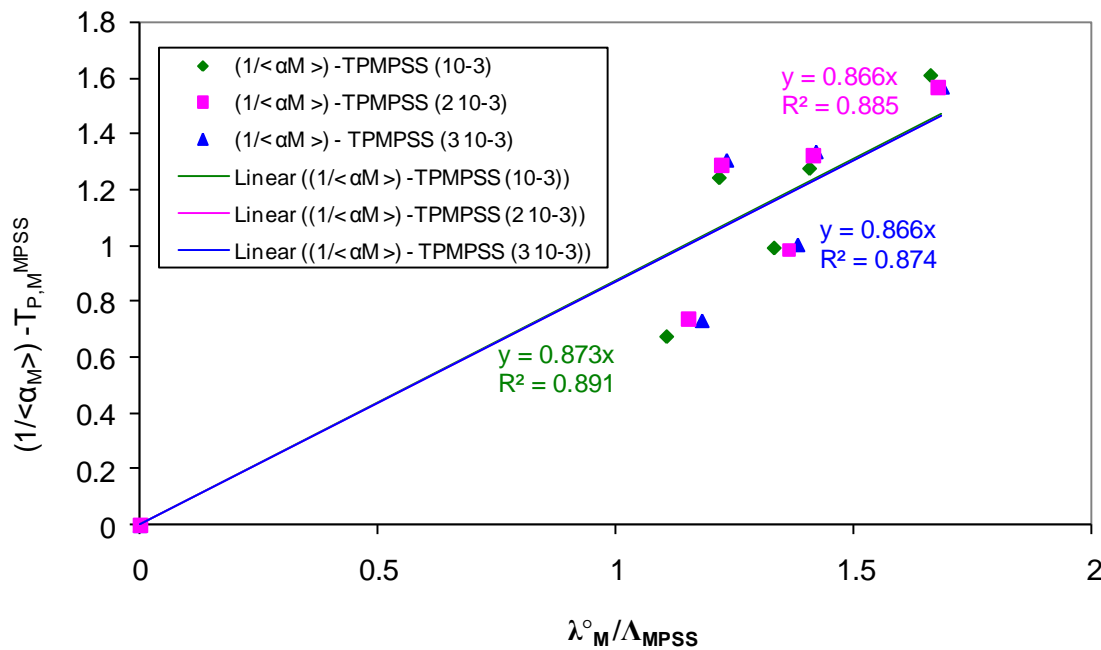


Figure 2. Variations of $y = (\langle \alpha_M \rangle^{-1} - T_{P,M})$ with $(\lambda_M^\circ / \Lambda_{MP})$ with $x = (\lambda_M^\circ / \Lambda_{MPSS})$, for three concentrations: 1 10⁻³ M, 2 10⁻³ M and 3 10⁻³ M, for different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

However, despite the apparent compatibility of the Vink's approach with the Manning's model, at least concerning the quasi-stability of the values α_M and $(1 - \beta_{ir})$, direct calculation according to Eq.16, of the "experimental" values of the conductivity $\lambda_{PSS,M}$ of the PSS polyion partially condensed by the counter-ions M, shows a significant dependence of $\lambda_{PSS,M}$ with the *nature* of the counter-ion M (see table 4a). This result is quantitatively and qualitatively in contradiction with the Manning's theory. Indeed, the values of $\lambda_P^{Manning}$, calculated according to Manning's equation (Eq. 6), are greater than their corresponding "experimental" values: $\lambda_{PSS,M}$ of about 60%. On the other hand $\lambda_P^{Manning}$ is independent on the nature of the counter-ions M. Table 4a and figure 3a, summarize all the results in the case of KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

Table 4a. Variation with the counter-ion concentration C_M^+ of: the experimental conductivity $\lambda_{PSS,M}$, the Manning conductivity $\lambda_P^{Manning}$, for different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

C_M^+ mol.l ⁻¹	$\lambda_{PSS,K}$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Na}$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Li}$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Et4N}$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Bu4N}$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_P^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹
5 10 ⁻⁴	66.075	67.358	61.016	52.926	45.485	110.889
1 10 ⁻³	63.618	63.058	57.357	50.423	41.783	102.995
1.5 10 ⁻³	61.445	59.541	54.291	48.277	38.945	98.377
2 10 ⁻³	59.500	56.794	51.811	46.466	36.921	95.100
2.5 10 ⁻³	57.771	54.840	49.975	44.998	35.639	92.558
3 10 ⁻³	56.248	53.636	48.686	43.834	35.054	90.482
3.5 10 ⁻³	54.966	53.178	48.027	42.961	35.180	88.726

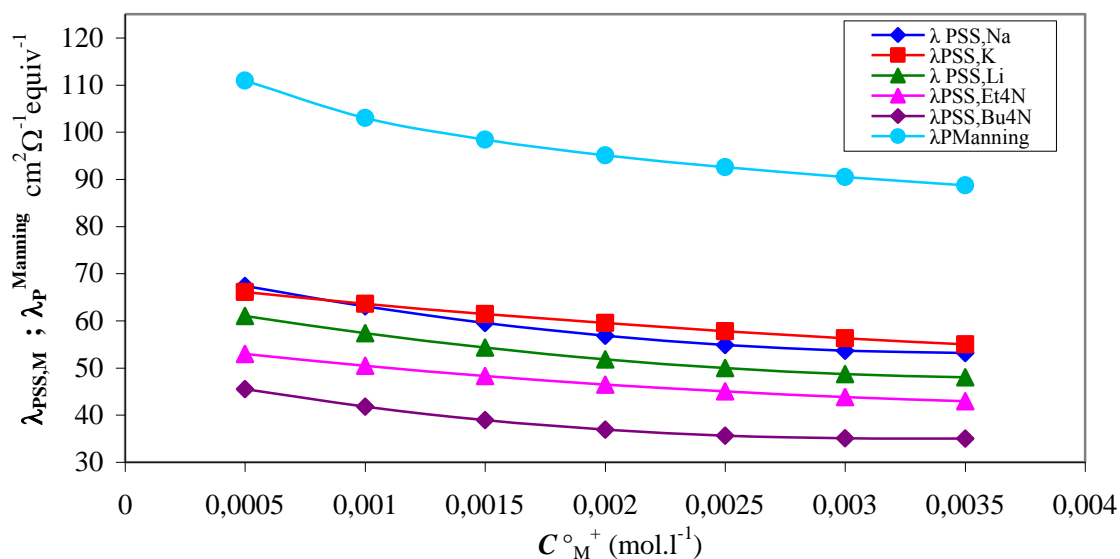


Figure 3a. Comparison between variations with the counter-ion concentration C_M^+ of: the experimental conductivity λ_{KPSS} ,

λ_{NaPSS} , λ_{LiPSS} , $\lambda_{Et4NPSS}$ and $\lambda_{Bu4NPSS}$, the Manning conductivity $\lambda_P^{Manning}$, for different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

Moreover, according to the previous Vink's approach, and with the assumption that both $\langle \alpha_M \rangle$ and $(1 - \beta_{ir})$ are *independent* on the counter-ion species, combination of Eqs. 16 and 20 lead to following expression of the *calculated* conductivity $\lambda_{P,M}^C$ of the PSS polyion in terms of these two parameters:



$$\lambda_{P,M}^C = (1 - \beta_{ir}) \lambda'_{P,M} = [\Lambda_{MP} / \langle \alpha_M \rangle] - \lambda^{\circ}_M (1 - \beta_{ir}) \quad (22)$$

Table 4b and figure 3b, summarize all the results in the case of KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C. Note that if Vink's approach is exact, the different $\lambda_{P,M}^C$ must be identical to their corresponding experimental values $\lambda_{PSS,M}$ given in table 4a. However, we note a non-negligible dispersion of the results.

Table 4b. Variation with the counter-ion concentration C_M^+ of: the calculated equivalent conductivities $\lambda_{PSS,M}^C$, the Manning conductivity $\lambda_P^{Manning}$ and the average degree of dissociation $\langle \alpha_M \rangle$, for different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

C_M^+ mol.l ⁻¹	$\langle \alpha_M \rangle$	$\lambda_{PSS,K}^C$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Na}^C$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Li}^C$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Et4N}^C$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_{PSS,Bu4N}^C$ cm ² Ω ⁻¹ equiv ⁻¹	$\lambda_P^{Manning}$ cm ² Ω ⁻¹ equiv ⁻¹
5 10 ⁻⁴	0.319	75.819	68.431	66.265	49.739	39.774	110.889
1 10 ⁻³	0.328	70.841	64.906	63.212	46.322	36.717	102.995
1.5 10 ⁻³	0.335	67.162	62.269	60.883	43.751	34.384	98.377
2 10 ⁻³	0.342	63.885	59.816	58.649	41.512	32.397	95.100
2.5 10 ⁻³	0.346	62.069	58.407	57.287	40.181	31.144	92.558
3 10 ⁻³	0.350	60.540	57.101	55.959	39.102	30.166	90.482
3.5 10 ⁻³	0.352	59.986	56.462	55.160	38.647	29.716	88.726

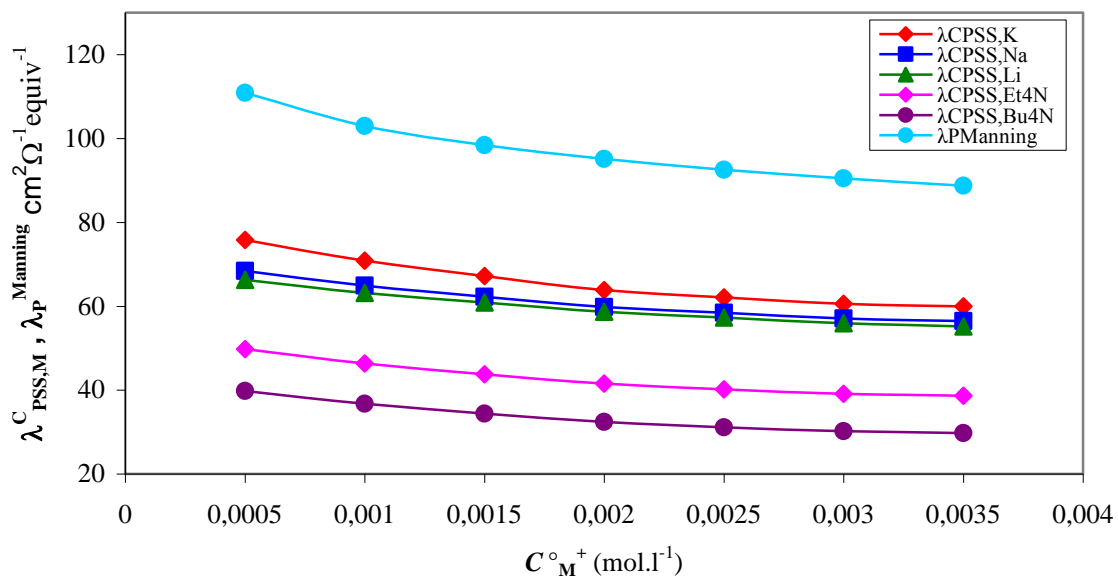


Figure 3b. Comparison between variations with the counter-ion concentration C_M^+ of: the calculated equivalent conductivities λ_{KPSS}^C , λ_{NaPSS}^C , λ_{LiPSS}^C , $\lambda_{Et4NPSS}^C$ and $\lambda_{Bu4NPSS}^C$, the Manning conductivity $\lambda_P^{Manning}$, for different Polystyrene Sulphonate MPSS: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

3.2 Vink's interpretation of the dependence of the experimental $\lambda_{PSS,M}$ with the nature of the counter-ions.

As indicated previously, the Manning's model is not able to explain the dependence of the polyion conductivity with the nature of the counter-ions M because the polyion is assumed to be an infinite thread and the counter-ions are modeled as punctual charges. In contrast, Vink suggests a more realistic description which offers an explanation of the dependence of the conductivity of the polyion with the size R_M of the condensed counter-ions species. Indeed, according to his model,



the hydrodynamic friction on the polyion increases with the minimal distance of approach ($R_{C,M} = R_C + R_M + nR_w$) between a condensed counter-ion and a charged polyion group. R_C is the radius of the polyion, R_w is the radius of water molecule and nR_w is a correction due to the hydration effect with: $n = 0, 1$ or 2 .

In the following section we will demonstrate that this interpretation is correct in its principle but it cannot explain the *important* decrease of $\lambda_{PSS,M}$ with the size R_M of the condensed counter-ions species (from K^+ to Bu_4N^+) which is of about 35%.

4. MODELING OF POLYION AS STRETCHED CHAIN OF CHARGED SPHERES

4.1 Conductivity of Stretched Polyelectrolyte in Dilute Solutions

The expression of the equivalent conductivity $\lambda_{P,M}$ of a polyion is in fact more complex because its ionic equivalent conductivity at infinite dilution λ_P^o expresses both hydrodynamic friction effect via λ_P^{oHyd} and dielectric friction effect via β_P^{dfi} [6]. For this reason, we can decompose $\lambda_{P,M}$ as follows:

$$\lambda_{P,M} = (\alpha_{CM}\lambda_P^{oHyd} - \Delta\lambda_P^{el}) / (1 + \beta_{ir}^P + \beta_P^{dfi}) = \lambda_P^{Henry} / (1 + \beta_{ir}^P + \beta_P^{dfi}) \quad (23)$$

α_{CM} is the degree of dissociation of the polyelectrolyte for which the polyion is modeled as a chain of charged spheres. λ_P^{oHyd} is the purely hydrodynamic contribution due to the viscosity η of the solvent, and $\Delta\lambda_P^{el}$ is the so-called electrophoretic effect which expresses the hydrodynamic friction on the ionic atmosphere of the polyion. β_{ir}^P is the ionic friction coefficient of the polyion.

4.1.1 Hydrodynamic friction and Electrophoretic effect

In previous works [6-8, 16, 17], we have noted that the first term ($\alpha_{CM}\lambda_P^{oHyd} - \Delta\lambda_P^{el}$) is identical to the expression of the Henry equivalent conductivity λ_P^{Henry} given by [6, 18]:

$$\lambda_P^{Henry} = \alpha_{CM}|Z_S|Fe / 6\pi\eta C'_{AP} \quad (24)$$

F is the Faraday, e is the proton charge and C'_{AP} is in fact the electrostatic Gouy capacitance (in c.g.s.u.e units) of the ellipsoidal (or cylindrical) capacitor constituted by the polyion and by its ionic atmosphere of mean radius $\langle d_P \rangle$. Eq. 24 is a generalization of the Stokes-Hubbard equation [19].

$$(C'_{AP})^{-1} = [\langle R_P \rangle^{-1} - \langle d_P \rangle^{-1}] ; \langle d_P \rangle = L_S / \text{Ln}[g(d_P, L_S)] ; \langle R_P \rangle = L_S / \text{Ln}[g(R_C, L_S)] \quad (25)$$

$\langle R_P \rangle$ is the mean radius of the polyion (analog to the radius of gyration) which is also equal to the electrostatic capacitance C_{AP} (in c.g.s.u.e units) of the ellipsoidal (or cylindrical) polyion [18, 19].

$$g(x, L_S) = [(4x^2 + L_S^2)^{1/2} + L_S] / [(4x^2 + L_S^2)^{1/2} - L_S] \quad (26)$$

$$d_P = R_C + 1/2\Gamma_{PMSA} \quad (27)$$

$g(x, L_S)$ is "the configuration function" which depends on the conformation of the polyion. The thickness d_P of the ionic atmosphere is a function of the radius R_C of the cylindrical chain and of α_{CM} and C_M^o via the Debye-MSA screen parameter Γ_{PMSA} [20] and the Debye length χ_D^{-1} .

$$2\Gamma_{PMSA} = [-1 + (1 + 4\chi_D R_M)^{1/2}] / 2R_M ; \chi_D^2 = 4\pi 10^{-27} N_A L_B (Z_M^2 \alpha_{CM} C_M^o) \quad (28)$$

Z_M is the valence of the counter-ion, R_M is the *effective* radius of the solvated counter-ion "M", N_A is the Avogadro number and L_B is the Bjerrum length.



4.1.2 Ionic friction on the polyion

Recall that in addition to the electrophoretic effect, one must take into account the ionic relaxation effect due to the polarization of the ionic atmosphere of the moving polyion by the external field. This local polarization induces a reacting relaxation field in order to moderate the perturbation caused by the external field. The result is a decrease of the mobility of the polyion when the concentration of the counter-ions increases via the ionic friction coefficient β_{ir}^P as indicated in Eq. 23. The expression of β_{ir}^P is given by [6-8]:

$$\beta_{ir}^P = \alpha_{CM} |Z_S Z_M| L_B (3d_P^2 + L_S^2/4) / [18(d_P^2 + L_S^2/4)^{3/2}] \tag{29}$$

Note that for a free salt polyelectrolyte, the ionic friction coefficient β_{ir}^P of the polyion is equal to the ionic friction coefficient β_{ir}^M of the counter-ions [6, 13]:

$$\beta_{ir}^P = \beta_{ir}^M \tag{30}$$

Note also that for spherical configuration: $L_S/d_P \rightarrow 0$, then: $\beta_{ir}^P \rightarrow \alpha_{CM} |Z_M Z_S| L_B / (6d_P)$, this limiting expression converges toward the Debye-Onsager relation applicable for spherical ions. In contrast, for polyions of very large length: $L_S \gg d_P$ and thus: $\beta_{ir}^P \rightarrow 1/9 \nabla C_M^0$ if $\alpha_{CM} \rightarrow \alpha^{Manning}$. Consequently, $(1 - \beta_{ir}^P) \rightarrow 0.889$, this limit is in conformity with both Manning and Vink approaches.

4.1.3 Importance of the Dielectric Friction Effect

In this paragraph we will discuss succinctly the dielectric frictional effect on a slowly moving polyion due to dielectric loss in its surrounding medium. Calculations of the dielectric frictional force on a charged sphere were performed successively by R. Zwanzig [15], J. Hubbard and L. Onsager [23] and P. G. Wolynes [21]. However, this dielectric effect is completely ignored by the Manning's model and it is not cited in the Vink's approach.

Indeed, the apparent charge ($\alpha_{CM} Z_S e$) of a polyion moving along Oz with a velocity v, induces a polarization of its surrounding dielectric medium which in turn creates after a relaxation time τ (delay) a dielectric frictional force F_z acting on the polyion. In fact, this force depends on the conformation (shape) of the polyion [6-8, 16-18]. In the case of a coiled polyion represented by an ellipsoidal conformation, the expression of F_z is [18]:

$$F_z = -(2/3)(v\tau)(\epsilon_0 - \epsilon_\infty)\epsilon_0^{-2}(\alpha_{CM} Z_S e)^2 (R_{app})^{-3} = -\xi^D v \tag{31}$$

The sign “-” expresses the fact that the direction of the frictional force is opposite to the direction of v. The factor (v τ) expresses the delay effect so that F_z vanishes for immobile polyion: v = 0, or in the case of instantaneous response: $\tau = 0$. ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants of the solvent and the $(\epsilon_0 - \epsilon_\infty)\epsilon_0^{-2}$ term expresses the dielectric saturation effect. R_{app} is the apparent radius of the polyion which depends on its eccentricity [18], and ξ^D is the translational dielectric friction related to the β_P^{dfi} coefficient via the Henry mobility $u_P^{Henry} = \lambda_P^{Henry} / F$, according to [18]:

$$\beta_P^{dfi} = |\alpha_{CM} Z_S e|^{-1} \xi^D u_P^{Henry} = (2/3)(u_P^{Henry} \tau)(\epsilon_0 - \epsilon_\infty)\epsilon_0^{-2} |\alpha_{CM} Z_S e| (R_{app})^{-3} \tag{32}$$

For coiled polyions, $\beta_P^{dfi} \ll 1$, because of the term $(R_{app})^{-3}$, and therefore according Eq. 23, the dielectric friction effect remains weak. It is interesting to note that when the *moving* polyion is assumed to be a thread of infinite length ($L \rightarrow \infty$) with a continuous linear charge (Manning's Model), so that the local distribution of its surrounding solvent molecules remains undisturbed, the polyion appears therefore as an equivalent *immobile* polyion (no dielectric friction).

In the specific case of a stretched polyion modeled as a chain of $|Z_S|$ identical spheres of charge $q_n = \alpha_{CM} e$ and of radius $R_{g,M}$ (a linear discontinuous distribution of ionized groups), each partially charged group undergone a dielectric friction effect proportional to $(R_{g,M})^{-3}$ and not to $(R_{app})^{-3}$ (with $R_{g,M} \ll R_{app}$) and consequently, the conformation transition from coiled state to stretched state will be accompanied by a sharp increase of the dielectric friction on the polyion. The corresponding expression of the dielectric friction coefficient β_P^{dfi} is therefore given by [17, 22]:

$$\beta_P^{dfi} = (2e\alpha_{CM}/3)(\tau u_P^{Henry} / |Z_S| b_S^3) [(\epsilon_0 - \epsilon_\infty)\epsilon_0^{-2}] (f_M^3 - 4.808) |Z_S| + 6.58] ; f_M = b_S / R_{g,M} \tag{33}$$

With, according to Eqs. (24 -28): $u_P^{Henry} = (e|Z_S| \alpha_{CM} / 6\pi\eta C_{AP})$. Now, if we replace the relaxation time τ by its Debye's expression: $\tau = (6\pi\eta R_w^3 / k_B T)$, with $L_B = e^2 / \epsilon_0 k_B T$, the general explicit expression of β_P^{dfi} becomes:



$$\beta_P^{\text{dfi}} = (2/3)\alpha_{\text{CM}}^2(R_w/b_S)^3(L_B/C'_{\text{AP}})[1 - \epsilon_\infty/\epsilon_0] |(f_M^3 - 4.808) |Z_S| + 6.58 | \quad (34)$$

In fact, the dielectric friction undergone by each spherical group can be decomposed into a self contribution due to the polarization induced by its own charge α_{CM} and into a crossed contribution due to the polarization caused by the other $|Z_S - 1|$ spherical groups (interference effect indicated by the index "i" in β_P^{dfi}). Notice however that, if the distance: $b_S = L_S/|Z_S|$, between two successive charged groups is sufficiently large, $f_M^{-1} \rightarrow 0$ and the interference effect vanishes.

It is interesting to note that β_P^{dfi} increases with dilution as α_{CM}^2 and it reaches its maximal value $\beta_P^{\circ\text{dfi}}$ at infinite dilution i.e. when $\alpha_{\text{CM}} \rightarrow 1$ (Ostwald) and $C'_{\text{AP}} \rightarrow \langle R_P \rangle$:

$$\beta_P^{\circ\text{dfi}} = (2/3)(R_w/b_S)^3(L_B/\langle R_P \rangle)[1 - \epsilon_\infty/\epsilon_0] |(f_M^3 - 4.808) |Z_S| + 6.58 | \quad (35)$$

Consequently, according to Eqs. (29, 33 and 34), the two friction coefficients: $\beta_{\text{ir}}^{\text{P}}$ (ionic friction) and β_P^{dfi} (dielectric friction), can be written respectively in terms of an ionic parameter B and of a dielectric parameter \mathbf{C}_M as follows:

$$\beta_{\text{ir}}^{\text{P}} = \alpha_{\text{CM}} B \quad ; \quad \beta_P^{\text{dfi}} = \alpha_{\text{CM}}^2 \mathbf{C}_M \quad (36)$$

With:

$$B = |Z_S Z_M| L_B (3d_P^2 + L_S^2/4) / [18(d_P^2 + L_S^2/4)^{3/2}] \quad \text{and} \quad \mathbf{C}_M \approx \beta_P^{\circ\text{dfi}} (\langle R_P \rangle / C'_{\text{AP}}) \quad (37)$$

Note that the dependence of α_{CM} and \mathbf{C}_M with the nature of the counter-ion is indicated by the index M.

In the other hand, the term $(\alpha_{\text{CM}} \lambda_{\text{P}}^{\circ\text{Hyd}} - \Delta \lambda_{\text{P}}^{\text{el}})$ expressing in Eq.23 the hydrodynamic contribution and the electrophoretic contribution can also be written in terms of the hydrodynamic parameter \mathbf{A}_M defined as follows:

$$(\alpha_{\text{CM}} \lambda_{\text{P}}^{\circ\text{Hyd}} - \Delta \lambda_{\text{P}}^{\text{el}}) = \alpha_{\text{CM}} |Z_S| F e / 6 \pi \eta C'_{\text{AP}} \equiv \alpha_{\text{CM}} \mathbf{A}_M \quad (38)$$

The introduction of Eqs. (36 and 38) into Eq. 23 leads to the following "Universal form" of the expression of the conductivity $\lambda_{\text{P},M}$ of the stretched polyion:

$$\lambda_{\text{P},M} = \alpha_{\text{CM}} \mathbf{A}_M / [1 + \alpha_{\text{CM}} B + \alpha_{\text{CM}}^2 \mathbf{C}_M] \quad (39)$$

We have used previously this general form in order to distinguish between the Manning's regime for which the degree α_{CM} remains quasi constant, and the Ostwald's regime for which $\lambda_{\text{P},M}$ varies more appreciably with the dilution process via α_{CM} [17, 22].

In this paper we will use this expression in order to explain the possible specific dependence of the conductivity $\lambda_{\text{P},M}$ of the polyion with the *nature* of the counter-ions. Indeed, According to Eq. 39, this specificity can result from the dependence with the nature of the counter-ion M, of α_{CM} , \mathbf{C}_M and \mathbf{A}_M parameters relating to respectively the process of ionic condensation, the dielectric friction (via the specific group radius $R_{g,M}$), and the hydrodynamic-electrophoretic friction.

Only the two parameters: α_{CM} and \mathbf{A}_M are considered in the Vink's approach. Moreover, the comparison for each concentration between the α_{CM} of the different counter-ions given in table 3, show that organic cations Et_4N^+ and Bu_4N^+ present a certain specific association with the charged groups of the PSS polyion due to their hydrophobic character. In contrast, ionic condensation of the alkaline cations Li^+ , K^+ and Na^+ seems to be quasi independent on the nature of the counter-ion and their mean value is equal to the Manning value which is about 0.35. Consequently, according to Vink's interpretation, the important deviations: $\Delta \lambda \equiv (\lambda_{\text{P},M} - \lambda_{\text{P},M'})$ observed between two polyion conductivities of any couple of counter-ions M and M' must be interpreted in terms of hydrodynamic friction parameter \mathbf{A}_M (via the *specific* cylindrical radius $R_{\text{CM}} = R_C + R_M + nR_w$). In contrast, it is obvious that this specificity disappears in the case of the Manning's Model. In the following paragraph, we will show that in the case of stretched polyion, the most important factor at the origin of the specificity of $\lambda_{\text{P},M}$ to M comes rather from the high sensitivity of the dielectric parameter \mathbf{C}_M to the local structure parameters characterizing the surrounding of each specific group of apparent radius $R_{g,M}$.



4.2 Interpretation of the dependence of the conductivity of PSS with the nature of the counter-ion.

In this section we will calculate for each counter-ion M of concentration C_M° the different specific parameters: R_{CM} , A_M , C_M and $R_{g,M}$ defined previously, in order to interpret the dependence of the conductivity of PSS with the nature of each counter-ion.

Table 5 gives the different ionic radii R_M and the different *specific* cylindrical radii $R_{CM} = R_C + R_M + R_w$ relating to the counter-ions Li^+ , K^+ , Na^+ , Et_4N^+ and Bu_4N^+ , using $R_C = 6.85 \text{ \AA}$ [17] (radius of the PSS chain) and $R_w = 1.4 \text{ \AA}$ (radius of the water molecule).

Table 5. Radii R_M and *specific* cylindrical radii R_{CM} relating to the counter-ions Li^+ , K^+ , Na^+ , Et_4N^+ and Bu_4N^+ .

	K^+	Na^+	Li^+	Et_4N^+	Bu_4N^+
$R_M \text{ (}\text{\AA}\text{)}$	1.33	0.98	0.68	4.0	4.94
$R_{CM} \text{ (}\text{\AA}\text{)}$	8.18	9.23	10.33	10.85	11.79

Calculation of the specific empirical parameters C_M which are related to the dielectric friction is achieved according to the following equation after recombination of Eq. 39:

$$C_M = [\alpha_{CM} A_M - \lambda_{P,M} (1 + \beta_{ir}^P)] / \alpha_{CM}^2 \lambda_{P,M} \tag{40}$$

The $\lambda_{P,M}$ indicates the experimental conductivity of PSS in presence of the counter-ion "M" (see table 4a). The expression of the hydrodynamic-electrophoretic parameter A_M is extracted from Eq. (38).

$$A_M = |Z_S| Fe / 6\pi\eta C'_{AP} \tag{41}$$

The capacity C'_{AP} is defined by Eqs. (25, 26, 27 and 28). Tables 6 gives the variations with the total ionic concentration C_M° of the hydrodynamic-electrophoretic parameters " A_M " and the dielectric parameters C_M relating to Polystyrene Sulphonate KPSS, NaPSS, LiPSS, Et_4NPSS and Bu_4NPSS in water at 25 °C.

Table 6. Variations with counter-ions concentration C_M° of the hydrodynamic-electrophoretic parameters " A_M " and the dielectric parameters C_M relating to Polystyrene Sulphonate: KPSS, NaPSS, LiPSS, Et_4NPSS and Bu_4NPSS in water at 25 °C.

C_M° mol.l ⁻¹	A_K	C_K	A_{Na}	C_{Na}	A_{Li}	C_{Li}	A_{Et4N}	C_{Et4N}	A_{Bu4N}	C_{Bu4N}
$5 \cdot 10^{-4}$	274.115	2.628	268.103	2.147	258.606	2.885	258.125	4.710	254.202	6.743
$1 \cdot 10^{-3}$	249.068	1.961	242.303	1.754	232.975	2.381	233.317	3.996	228.801	6.421
$1.5 \cdot 10^{-3}$	234.376	1.674	227.029	1.670	217.822	2.239	218.800	3.724	213.916	6.469
$2 \cdot 10^{-3}$	223.902	1.527	216.184	1.651	207.068	2.194	208.495	3.595	203.495	6.523
$2.5 \cdot 10^{-3}$	215.723	1.444	207.883	1.606	198.849	2.144	200.502	3.506	195.637	6.459
$3 \cdot 10^{-3}$	208.990	1.391	201.275	1.497	192.292	2.060	193.969	3.418	189.486	6.219
$3.5 \cdot 10^{-3}$	203.255	1.341	195.907	1.301	186.992	1.899	188.445	3.308	184.609	5.768

According to this table we can conclude that:

- The hydrodynamic-electrophoretic friction increases with the R_{CM} radius of the condensed counter-ion, from K^+ to Bu_4N^+ (see table 5). However, this increase cannot, completely explain the great dependence of the conductivity of the polyion with the nature of its counter-ion.



- The dielectric friction is practically the same for Na⁺ and K⁺, it undergoes a weak increase for Li⁺ and it increases by a factor two for Et₄N⁺ and by a factor three for the Bu₄N⁺.

In order to interpret the dependence of C_M with the nature of the counter-ions, we will express the parameter C_M in terms of the physical parameters influencing the dielectric friction effect (i.e. the dielectric relaxation time τ, the local dielectric permittivities ε_o and ε_∞ around each group). Combination of Eqs. (33 and 36), leads to:

$$C_M = (e^2/9\pi\eta) (1/C'_{AP} b_S^3) [T (\epsilon_o - \epsilon_\infty) \epsilon_o^{-2}] [(f_M^3 - 4.808) |Z_S| + 6.58] ; f_M = b_S / R_{g,M} \tag{42}$$

Eq. 42 can be recombined in order to express the group radius R_{g,M} as a function of τ:

$$R_{g,M} = b_S [9\pi\eta C_M C'_{AP} b_S^3 \epsilon_o^2 \{e^2 |Z_S| T (\epsilon_o - \epsilon_\infty)\}^{-1} + 4.808 - 6.58/|Z_S|]^{-1/3} \tag{43}$$

Calculation of R_{g,M} needs the knowledge of the relaxation time τ of water molecules, the static permittivity ε_o and the high-frequency permittivity ε_∞ of water. Experimental values of τ, ε_o and ε_∞ for pure water at 298.15 K are: ε_o = 78.3, ε_∞ = 4.49 and τ = 8.32 ps [24]. Note that this last value is less than the value estimated according to the Debye's expression: τ = (6π²R_w³/k_BT) = 11.187 ps at 298.15 K. Table 7 gives the variations with the total ionic concentration C^o_M of the calculated group radii R_{g,M} in Å°, relating to Polystyrene Sulphonate KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C. One indicates by < R_{g,M} >, the mean group radius of the polyion PSS partially condensed by counter-ions M. The Examination of these results shows that the obtained mean radii: < R_{g,M} >, depend on the nature of the counter-ions and are in general greater than the structural group radius of the PSS polyion which is equal to R_g = b_S/2 = 1.25 Å°. Deviation of < R_{g,M} > from R_g can be interpreted by replacing τ and ε_o in Eq. 43 by their "local" values τ' and ε'_o. Indeed, the relaxation time of water molecules around the polyion PSS and its counter-ions is different from its bulk value τ, so that τ' is in fact a mean value < τ. In same way, ε'_o < ε_o because of the dielectric saturation effect in the surrounding of the polyion and the counter-ions. It is obvious that the local structure of water depend on the nature of the surrounding counter-ions, this could explain the specificity of the dielectric parameter C_M to the nature of counter-ions via τ' and ε'_o.

Table 7. Variations with counter-ions concentration C^o_M of the the group radii R_{g,M} in Å° and < R_{g,M} > are the mean group radii, relating to Polystyrene Sulphonate: KPSS, NaPSS, LiPSS, Et₄NPSS and Bu₄NPSS in water at 25 °C.

C ^o _M mol.l ⁻¹	R _{g,K}	R _{g,Na}	R _{g,Li}	R _{g,Et4N}	R _{g,Bu4N}
5 10 ⁻⁴	1.350	1.370	1.335	1.265	1.203
1 10 ⁻³	1.372	1.378	1.345	1.275	1.193
1.5 10 ⁻³	1.381	1.379	1.346	1.276	1.178
2 10 ⁻³	1.385	1.375	1.343	1.274	1.167
2.5 10 ⁻³	1.387	1.375	1.341	1.272	1.161
3 10 ⁻³	1.388	1.378	1.342	1.271	1.162
3.5 10 ⁻³	1.389	1.388	1.348	1.272	1.162
< R _{g,M} >	1.378	1.377	1.343	1.272	1.175

5. CONCLUSION

The Manning's model is not able to explain the dependence of the conductivity of the PSS polyion with the nature of the counter-ions M, because the counter-ions are assumed as punctual charges. However, predictions according to this model of both the degree of condensation and the ionic friction coefficient (α ≈ 0.35 and β_{ir} ≈ 0.13) are acceptable in particular for the alkaline cations (Li⁺, Na⁺ and K⁺), but with a small observed negative deviation (α ≈ 0.31) for the two hydrophobic cations (Et₄N⁺ and Bu₄N⁺).

In contrast, Vink has suggested a more realistic qualitative description in taking into account of the cylindrical radius R_C of the polyion and the size R_M of the condensed counter-ions, so that the hydrodynamic friction on the polyion increases with the minimal distance of approach (R_{C,M} = R_C + R_M + nR_w) between a specific condensed counter-ion and a charged polyion group.

In this work, we have used a recent model in which the stretched PSS polyion is represented by a chain of successive charged spheres, partially condensed by the counter-ions, in order to quantify the dependence of the hydrodynamic



friction on PSS polyion with the size of alkaline cations (Li^+ , Na^+ and K^+) and with the size of two hydrophobic cations (Et_4N^+ and Bu_4N^+), and we have found that the moderate increasing of this friction with the R_{CM} distance from K^+ to Bu_4N^+ , cannot completely explain the *important* decrease (of about 35% from K^+ to Bu_4N^+) of the conductivity ($\lambda_{\text{PSS,M}}$) of the PSS polyion with the size R_{M} of its condensed counter-ion M. Consequently, we have proposed a supplementary explanation to the high dependence of the mobility of the polyion with the nature of its counter-ions, by taking into account of the translational dielectric friction on the moving polyion due to the time dependent polarization of its surrounding water molecules. This supplementary friction which is in the case of this model, the most important friction effect, can be evaluated quantitatively in terms of the specific dielectric parameter \mathbf{C}_{M} which is function on the relaxation time τ of water molecules, the static permittivity ϵ_0 and the high-frequency permittivity ϵ_∞ of water. Now, as these physical parameters are sensitive to the local structure of water surrounding the polyions, and in turn, this local structure depends on the nature of the condensed counter-ions, we suggested that the specificity of the parameter \mathbf{C}_{M} could explain the high dependence of the mobility of the polyion with the nature of its counter-ions.

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