# Notes

## Improvement in Conductometric Analysis of Metal/Polyelectrolyte Systems

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Conductometry has become an important tool in the analysis of counterion distributions in metal/polyelectrolyte solutions.[1−7] Conductometry measures the transport of all charged species in the system studied. The conductance of polyelectrolyte solutions is affected by association of counterions with the polyion. However, due to the lack of adequate theory, for quite some time the interpretation of conductivity data has remained mainly descriptive. In the seventies, substantial progress had been made in the development of the theory of polyelectrolytes, in particular with respect to counterion binding and conductivity.[8−10] For monovalent counterions, it is now possible to estimate the distribution of counterions over the free and bound states by varying the nature of the counterion.[8] One may formally express the molar conductivity $\Lambda$ of a salt-free polyelectrolyte solution as

$$\Lambda = f(\lambda_1{}^0 + \lambda_p) \tag{1}$$

where $\lambda_1{}^0$ and $\lambda_p$ represent the ionic conductivities of the free counterion in pure solvent and the polyion, respectively, and where $f$ is a parameter ($0 \leq f \leq 1$) which expresses the extent of reduction of the conductivity due to association between the counterions and the polyion. In terms of a two-state representation of the counterion distribution, one might refer to $f$ as the "conductometrically free" fraction of counterions. This is helpful in practice, but it should not lead us to ignore the real situation where the degree of interaction between the polyion and the counterions gradually varies as a function of distance. In the most general situation, where counterion condensation may occur, the counterion distribution is characterized by the range

electrostatically trapped ("condensed") by polyion
(if sufficiently charged) → constituent of diffuse
counterionic atmosphere → free ion at infinite
distance from polyion

In the case of a salt-free polyelectrolyte system, the state of the free ion is just the limit for the "outer" ions in the counterionic atmosphere.

One of the main issues in treating the conductivity of polyelectrolyte solutions is the quantification of the contribution from the ions in the diffuse counterionic atmosphere. Manning[11] tackled this by starting from the Nernst−Planck equation for the migration of the counterions, taking into account the radial part of the inhomogeneity of the electric field around the linear polyions and the steady ionic movement under the influence of the external field. Ignoring the possible mobility of condensed counterions along the chain, it was found that for $\xi \geq |z^{-1}|$.

$$f_i = 0.866|z_i{}^{-1}|\xi^{-1} \tag{2}$$

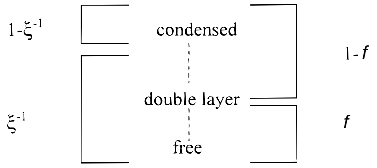
where $z_i$ is the valency of the counterion and $\xi$ is the structural charge density parameter. The dimensionless coefficient 0.866 results from the numerical evaluation of the components of the radially inhomogeneous electric field around the linear polyion with smeared-out charge. For polyions with $\xi < 1$ and monovalent counterions, the functionality of $f$ is

$$f_1 = 1 - \frac{0.55\xi^2}{\pi + \xi} \tag{3}$$

At this point it is useful to emphasize the difference between condensed counterions and conductometrically bound counterions. According to the counterion condensation concept,[11] systems are thermodynamically unstable if the charge density exceeds a certain critical value $\xi_{\text{crit}}$ which is equal to $|z^{-1}|$. The instability is resolved by association of counterions with the polyelectrolyte chain to such an extent that the net value of $\xi$ is reduced to the critical value. The condensed fraction, $r_i$, then equals

$$r_i = z_i{}^{-1}(1 - 1/z_i\xi) \tag{4}$$

and hence the remaining fraction $1 - r_i$ includes both the ions in the diffuse double layer and the free ions. The conductometrically bound ions include (at least in Manning's theory) all condensed ions, plus some part of the diffuse layer ions. Thus, in the case of monovalent counterions, the "free fraction" $f$ is always some fraction of $\xi^{-1}$ and the bound fraction $(1 - f)$ is always larger than $(1 - \xi^{-1})$. In the following scheme



(5)

the expressions for $f$ may be used in combination with eq 1 and thus serve as analytical working equations. The above described treatment is derived for very long rigid linear polyelectrolytes. The aim of the present note is to show the improvement that is obtained in the conductometric analysis of metal/polyelectrolyte systems by introducing the concept of flexibility of the macro-

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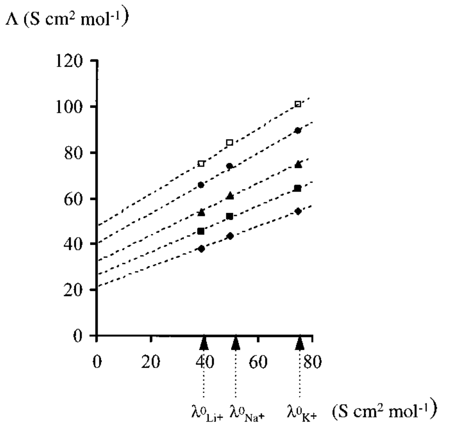

**Figure 1.** Plot of the molar conductivity of alkali polymethacrylate solutions vs the molar conductivity of the corresponding monovalent counterion for various charge densities of the polymethacrylate anion with [PMA]= 2.5 × $10^{-3}$ mol $L^{-1}$. $\xi$ = 0.91 (□); 1.14 (●); 1.48 (▲); 1.82 (■); 2.28 (◆).

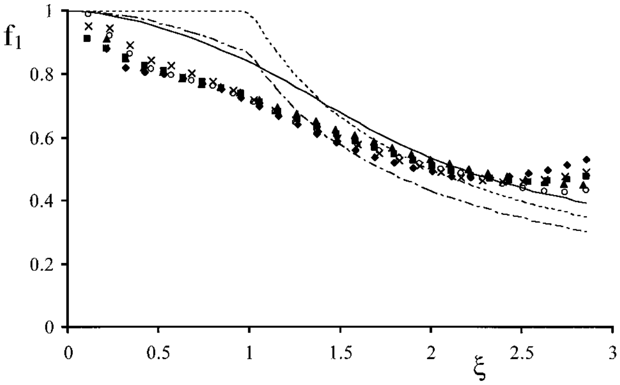

**Figure 2.** Experimental values (symbols) and theoretical values of $f_1$ as a function of $\xi$ for various concentrations of PMA. Key: dotted curve, free counterions according to the CC approach (cf. eq 4); dashed curve, conductometrically free counterions for rigid polymer (cf. eqs 2 and 3); solid curve, conductometrically free counterions for flexible polymer ($k$ = 22.6 kcal $mol^{-1}$ $nm^{-2}$). [PMA] = 0.8 × $10^{-3}$ mol $L^{-1}$ (◆); 1.35 × $10^{-3}$ mol $L^{-1}$ (■); 1.9 × $10^{-3}$ mol $L^{-1}$ (▲); 2.5 × $10^{-3}$ mol $L^{-1}$ (×), and 5.0 × $10^{-3}$ mol $L^{-1}$ (○).

molecule. This improvement is shown to be both qualitative and quantitative, especially for higher charge densities.

Several polymethacrylic acid (PMA) solutions were titrated with LiOH, NaOH, and KOH solutions, respectively, in the absence of additional salt. In Figure 1, plots of the molar conductivity of the polyelectrolyte solution Λ vs $\lambda_1^0$, the so called Eisenberg plots[1] are presented for various values of $\xi$ with [PMA]=2.5 × $10^{-3}$ mol $L^{-1}$. In accordance with eq 1, a straight line is obtained, indicating that the interaction of alkali metal ions and the polymethacrylate anion is of a nonspecific nature. The slopes and the intercepts of the lines in Figure 1 equal $f_1$ and $f_1\lambda_p$, respectively.

In Figure 2, the resulting experimental $f_1$ values are presented as a function of $\xi$ for various concentrations of PMA. The independence of $f_1$ with respect to the PMA concentration confirms the typical polyelectrolytic behavior of the alkali polymethacrylate system. In Figure 2, the dashed curve represents the fraction of conductometrically-free monovalent counterions computed with eqs 2 and 3, whereas the dotted curve equals the fraction of free counterions according to the condensation approach under salt-free conditions, i.e. $1 - r_1$. Note that both theoretical curves differ from the experimental data with respect to the discontinuity at $\xi = 1$.

The two theoretical curves correspond to very long and rigid linear polyelectrolytes. In order to compare the experimental data with theoretical calculations, we should take into account that the experimental data are the result of a thermodynamic average over all the conformations that the polymer can take in solution. A procedure has been used to obtain the proper thermodynamic average of the calculated fraction of conductometrically free counterions.[12] The starting point is that the (long) polymer is made of a large number of segments (Kuhn segment representation)[13] of an equal number of polymeric units ($N_s$) whose length follows a Gaussian distribution.[12] This distribution implies a Hookian behavior of the polymer segments around the equilibrium length. The thermodynamic (solution) average of the fraction of conductometrically free monovalent counterions is obtained as

$$\langle f_1 \rangle = \int W(r) f_1(r)\, \mathrm{d}r \tag{6}$$

where

$$W(r) \propto \exp[-(G^{\text{ion}} + G^{\text{conf}})/RT] \tag{7}$$

is the distribution of segment lengths, and $f_1(r)$ is the fraction of conductometrically free monovalent counterions that corresponds to a rigid polyelectrolyte with a charge density equal to the charge density of the segment of end-to-end length $r$; i.e., $b(r) = r/N_s$ if we assume one ionizable charge group per polymeric unit ($b$ = the structural value of the intercharge distance). In this way each polymer segment contributes to the measured (thermodynamic) value of $f_1$ according to each charge density. For the conformational free energy the Hookian form is used

$$G^{\text{conf}} = k(r - r_o)^2 \tag{8}$$

where $k$ is a constant related to the rigidity of the macromolecule and $r_o$ is the equilibrium length of the polyelectrolyte segment. For the present case, we estimated the rigidity of the PMA by adjusting the experimental titration curve in water.[14] Using $b = 0.25$ nm and $N_s = 20$, we have $r_o = 5$ nm. An excellent fit to the experimental titration curve is obtained using $k$ = 22.6 kcal $mol^{-1}$ $nm^{-2}$. Using these parameters, values for $f_1$ were calculated using eq 6, resulting in a curve with a *continuous* derivative. Hence, the agreement between experimental and predicted data has been improved qualitatively as well as quantitatively. This is especially the case for higher values of $\xi$, i.e. larger than 1.

For $\xi$ values smaller than 1, the agreement between experimental values and theoretical ones is certainly less. In this region PMA undergoes a hydrophobic transition as has been extensively described in the literature [e.g., refs 15−17], which complicates a proper description for this range of $\xi$ values. In addition, for very low values of $\xi$, the concentration of free protons may be rather high ($10^{-4}$ mol $L^{-1}$) and, hence, their contribution to the overall conductance may become substantial, which is not taken into account in the Eisenberg analysis. For very high values of $\xi$, the contribution of free hydroxyl ions to the conductivity starts to come into play. However, under these conditions the problem is less severe, since the molar conductivity of $OH^-$ is much smaller than that of $H^+$.

It is concluded that introduction of the concept of flexibility of macromolecular ligands into the conductometric analysis of metal/polyelectrolyte solutions improves the agreement between experimentally obtained fractions of conductometrically free ions and predicted ones. For the PMA polymer this is certainly the case for higher values of the polyelectrolytic charge density, whereas due to hydrophobic transition the agreement is less successful at low charge densities.

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