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V. Raicu
A. Băran
A. Iovescu
D.F. Anghel
S. Saito

Electrical conductivity of aqueous polymer solutions

1. Theory and experimental verification

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Dr. V. Raicu (✉)
Biotechnology Group
R&D Institute for Rare
and Radioactive Metals
Str. Atomistilor 51, Sect. 5
76920 Bucharest, Romania

A. Băran · A. Iovescu · D.F. Anghel
Department of Colloids
Romanian Academy
Institute of Physical Chemistry
Spl Independentei 202
79611 Bucharest, Romania

S. Saito
Nigawa-Takamaru 1-12-15
Takarazuka 665, Japan

Abstract Theoretical equations were proposed to adequately simulate the electrical conductivity behavior of aqueous solutions of both charged and uncharged polymers. The theory, based on the mixture equation of Boned and Peyrelasse, was experimentally verified on poly(acrylic acid) (PAA) in water and poly(ethylene oxide) (PEO) in aqueous electrolyte solutions. The data analysis suggested that both the polymer coils may be depicted as oblate ellipsoids. Subsequently, the semiaxes values of the polymer coils were determined, and they were in good agreement with the results reported in the literature.

Key words Electrical conductivity – electrical mobility – mixture equations – poly(acrylic acid) – poly(ethylene oxide)

Introduction

Conductivity measurements are widely used to characterize disperse systems, such as biological and non-biological macromolecules [1, 2] and micellar systems [3–5]. The analysis of experimental data generally makes use of the theoretical [6–10] or semi-empirical [1] mixture equations. The choosing of one or the other must take into account the shape of dispersed particles and their concentration in solutions. An overview of the theoretical mixture equations is given in the first part of the theoretical section of this paper.

The present paper reveals that the mixture equation of Peyrelasse and Boned [10] is the most suitable for analyzing the conductivity data obtained on both spherical and non-spherical polymer particles. This equation is also useful in that it holds up to very high volume fractions of dispersed particles.

The paper also proposes simple equations and approximations, which are suitable for ionic polymer solutions. In a particular case, they can be used to describe the behavior of nonionic polymers. The theory applied to analyze the originally data and some literature data [2]. In this respect, aqueous solutions of poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) [2] were investigated. The shape, dimensions and the hydration degree of the polymer coil were derived. The PEO/water system has been chosen because the literature data are available, while the PAA is known to interact with non-ionic surfactants [11–14], a field in which we are particularly interested.

Theory

Electrical conductivity of colloidal dispersions

Electrical conductivity of heterogeneous systems is given by mixture equations relating the bulk properties of the dispersed and continuum phases to those of the solution regarded as a whole. For dilute mixtures of spherical particles, the classical theory of Maxwell [6] and Wagner [7] gives the following expression:

$$\sigma = \sigma_m\left(1 - \frac{3}{2}\,\frac{\Phi(\sigma_m - \sigma_p)}{\sigma_p + 2\sigma_m + \Phi(\sigma_m - \sigma_p)}\right) \tag{1}$$

where σ_m and σ_p are the conductivity of suspending medium and of dispersed particles, respectively, and Φ is the volume fraction of the dispersed phase.

To adequately simulate dielectric properties of highly concentrated dispersions of spherical particles, Bruggeman [8] derived an equation that is also valid for electrical conductivity [15]. The Bruggeman's effective medium theory (EMT), based on the assumption of regularly arranged particles was further refined by Landauer [16], who considered that the dispersed particles are distributed at random in the host medium. However, further theoretical and experimental works have shown that the classical EMT gives a percolation threshold (i.e., the concentration at which a phase transition occurs in the system) which is much smaller than the one predicted by the percolation theory [17]. To reconcile the two theories, Granqvist and Hunderi [18] extended the EMT by incorporating the dipole–dipole interactions. This theory properly describes the clustering of dispersed particles, and gives a percolation threshold in agreement with numerical simulations based on the percolation theory.

Since dispersed particles are only rarely spherical, Bruggeman's equation fails to describe the data obtained in some measurements on aqueous polymer solutions and micellar systems [2, 5]. A more general mixture equation, initially derived by Looyenga [9], was subsequently proven to apply for concentrated dispersions of particles of any shape [2]. Nevertheless, the Looyenga equation can only yield the radius of the sphere of equal volume with that of the particle, and consequently, it is not very useful when one is trying to find the shape and dimensions of the dispersed particles. Under such circumstances, the mixture equation (of a Bruggeman type) for randomly oriented spheroids [10] seems to be more appropriate for interpreting the data on concentrated dispersions of non-spherical particles. This equation reads:

$$(1 - \Phi) = \left(\frac{\sigma_m}{\sigma}\right)^{3d}\left(\frac{\sigma - \sigma_p}{\sigma_m - \sigma_p}\right)\left(\frac{\sigma_m(1 + 3A) + \sigma_p(2 - 3A)}{\sigma(1 + 3A) + \sigma_p(2 - 3A)}\right)^{3k}$$

$$d = A(1 - 2A)/(2 - 3A)$$

$$3k = 2(1 - 3A)^2/((2 - 3A)(1 + 3A)) \tag{2}$$

where A is the shape-dependent depolarization factor. For spheroidal particles having the semiaxes $a \neq b = c$, the depolarization factor must satisfy the following equation [10, 19]:

$$A = \frac{ab^2}{2}\int_0^\infty \frac{ds}{(a^2 + s)^{3/2}(b^2 + s)}\,. \tag{3}$$

For prolate spheroids ($a > b = c$)

$$A = \frac{1}{1 - \alpha^2} + \frac{\alpha}{(\alpha^2 - 1)^{3/2}}\ln(\alpha + (\alpha^2 - 1)^{1/2}) \tag{4}$$

and for oblate spheroids ($a < b = c$)

$$A = \frac{1}{1 - \alpha^2} + \frac{\alpha}{(1 - \alpha^2)^{3/2}}\arccos(\alpha) \tag{5}$$

where α is the ratio of semiaxes (a/b).

For spherical particles ($a = b = c$), Eq. (3) gives a depolarization factor of 1/3. In such a case, the exponents in Eq. (2) take the values $d = 1/9$, $k = 0$ and Eq. (2) reduces to the Bruggeman equation [8].

In order to obtain the dispersed phase-related parameters from the measured suspension conductivity, the conductivity of external phase, σ_m, has to be known. In the approach presented here, we will consider the general case in which this quantity is not accessible to any direct measurements, but some physico–chemical characteristics of the system are known.

Let us consider a suspension of charged polymer in water. The conductivity of external medium is given by the equation:

$$\sigma_m = \sum_i n_i\,|Z_i|\,e\mu_i + n_c q_c \mu_c \tag{6}$$

where q_c is the charge of a polymer coil ($q_c = |Z_c|\,e$), n is the number of charge carriers per unit volume of solution, Z and μ are their valence and electrical mobility, and e is the electronic charge. Subscripts i and c refer to the species of small ions in solution and the polymer coil, respectively. The small ions may appear either from the dissociation of the polymer ionizable groups or by electrolyte adding.

Electrical mobility of charged colloidal particles

While the contribution of light ions to the σ_m is completely described by the first term in the right-hand side of Eq. (6), the contribution of the polymer coil needs further assumptions. It is thus necessary to derive an explicit equation for the mobility of polymer coil. We next calculate this quantity by following the line proposed by Schwan et al. [20].

A charged particle moving in alternating electrical field, $E = E_0 e^{j\omega t}$ (with ω the angular frequency of applied field), must satisfy the differential equation:

$$m_c \frac{dv}{dt} + r \cdot v = q_c \cdot E \tag{7}$$

where m_c is the mass of the macroion, v is its velocity, and r is the frictional coefficient (for spherical particles $r = r_0 = 6\pi\eta R$). Under steady state conditions, $v = v_0 e^{j\omega t}$ and Eq. (7) becomes:

$$\mu^* = \frac{q_c}{r} \cdot \frac{1}{1 + j\omega\tau} \tag{8}$$

where μ^* is the complex electrical mobility of the charged particle (i.e., v/E), and τ is a time constant denoting the quantity m_c/r. The imaginary part of Eq. (8) contributes to the equivalent dielectric constant of the solution, while the real one is related to the conductivity of the system. The real part of electrical mobility is given by

$$\mu_c = \frac{q_c}{r} \cdot \frac{1}{1 + \omega^2\tau^2} \tag{8'}$$

and, as can be readily seen, it is a frequency-dependent quantity. This is equivalent to say that the conductivity of the solution will exhibit dispersion in the frequency range of the same order of magnitude as the relaxation frequency of the system ($\omega_r \equiv 1/\tau = r/m_c$). To avoid too much theoretical and practical complication, in the present paper we are only interested to study the limiting conductivity at low frequency, namely the static conductivity. In this case, electrical mobility of the macroion takes a simpler form ($\mu_c = q_c/r$) that, introduced into Eq. (6), gives:

$$\sigma_m = \sum_i n_i |Z_i| e\mu_i + n_c \frac{qc^2}{r} . \tag{9}$$

Equations (2), (3) and (9) can form the basis for finding the shape and dimensions of a polymer coil, provided that the polymer content may be varied over a reasonable range of concentrations (see the next section). Since its applicability is restricted to low frequency only, the validity of Eq. (9) must be always checked by ensuring that the measured conductivity of the system under study is constant in the frequency range used. This is especially required when, for avoiding experimental artifacts (such as polarization of electrodes), relatively high frequencies are employed in measurements. If, for technical reasons (e.g., fixed frequency of measurements), it is not possible to investigate the system over a wide frequency range, there is still a way to check the appropriateness of using Eq. (9) to analyze the data. In this respect, it is possible to estimate the relaxation frequency (defined above) of the polymer system, by using known values for the mass of polymer coil and medium viscosity, and reasonable values for the polymer coil equivalent radius. If the measured frequency is much lower than the calculated relaxation frequency (i.e., $\omega \ll \omega_r$), Eq. (9) may be safely applied in interpreting the experimental data.

Approximate equations applicable to polymer solutions

On analyzing Eqs. (2) and (9), one may readily observe that the theory is somewhat more general than needed in practical problems. Therefore, simplified equations, regarding the polymer systems, will be derived below.

Considerations upon σ_m

Let us consider a polyacid in water, having the degree of polymerization g and the concentration C_m (expressed in mole of monomer per m^3 of solution). The polymer coils become charged, by releasing protons in water, and their charge is assumed to be entirely exposed on the coil surface. Let the concentration and mobility of released protons be C_{H^+} (mole/m^3) and μ_{H^+}, respectively. Taking into account the condition of solution electroneutrality,

$$C_{H^+} \cdot e = \frac{C_m}{g} \cdot q_c \tag{10}$$

and considering the case of no added salts, Eq. (9) becomes:

$$\sigma_m = C_{H^+} F \left(\mu_{H^+} + \frac{C_{H^+}}{C_m} e \frac{g}{r} \right) \tag{11}$$

where F is Faraday's number.

For solutions of uncharged polymers, it is obvious that the second term in Eq. (9), accounting for the electrical migration of charged particles, vanishes, and only the added electrolyte will make a contribution to σ_m. The same assumption is also true in the case of charged polymer, if the mobility of the polymer coil is negligibly small as compared to the light ions ones. Under both situations the medium conductivity may either be calculated (for low ion concentrations) or be experimentally determined.

The mixture equation

It is, generally, acceptable that the intrinsic conductivity of the polymer coil, σ_p, is negligibly small as compared to the external medium conductivity. Taking this statement into account, Eq. (2) may be rewritten as

$$\sigma = \sigma_m (1 - \Phi)^{1/L}$$

$$L = 6A(1 - A)/(1 + 3A) . \tag{12}$$

Depending on what is known in a given experiment (i.e., the dry volume fraction, Φ_0, or the monomeric molar concentration, C_m), the volume fraction, Φ, in Eq. (12) may be replaced by two alternate expressions:

$$\Phi = \Phi_0 \frac{V}{V_0} \tag{13a}$$

$$\Phi = \frac{C_m N_A}{g} V \tag{13b}$$

where V and V_0 are the coil hydrated volume and the dry volume, respectively, and V/V_0 is the hydration coefficient (h).

It must be remarked that in the most general case of ionic polymers the macroion gives two different types of contributions to the measured solution conductivity. Firstly, the macroion increases the system conductivity because of its proper electrical mobility, as expressed mathematically by Eq. (11). Secondly, the macroion obstructs the free migration of small ions in electrical field, and the conductivity decreases by a factor dependent on the concentration and shape of dispersed particles (the parentheses in Eq. (12)). At the same time, the non-ionic polymers act only as obstructants for the migration of small ions added to the system.

Experimental

The poly(acrylic acid) was purchased from Wako Pure Co. Ltd., Tokyo, Japan, and had the same characteristics as previously described [12]. It was used after a supplementary purification, by dialysis against doubly distilled water, using a cellophane membrane. The dialyzing time was 2 days, the medium being exchanged twice a day. The water used to prepare the solutions had an electrical conductivity lower than 2 μS/cm.

The pH measurements were made with an Orion pH-meter (model 420 A). The measuring error was less than 0.5%.

The conductivity measurements were carried out with an open-ended coaxial probe [21] connected to an impedance analyzer (Hewlett-Packard Model 4194 A). The measuring probe has been calibrated with saline solutions of known conductivity and permittivity [22], according to the method previously described [21]. In order to avoid electrode polarization, relatively high frequency range was chosen (1–10 MHz). The impedance analyzer was settled on 256 measurements on each polymer sample, and the final data were obtained as a mean over all the 256 values. The measured conductivity was nearly constant over the whole frequency range investigated. The accuracy of conductivity data was within 1% for all the samples.

All the measurements were performed at 20.0 ± 0.2 °C.

Results and discussions

Aqueous solutions of PAA

Figure 1 shows the measured proton concentration plotted against the molar concentration of the acrylic acid. The C_{H^+} data were simulated with a second-degree polynomial function, and the best fitted theoretical parameters were given in the legend of Fig. 1. In the

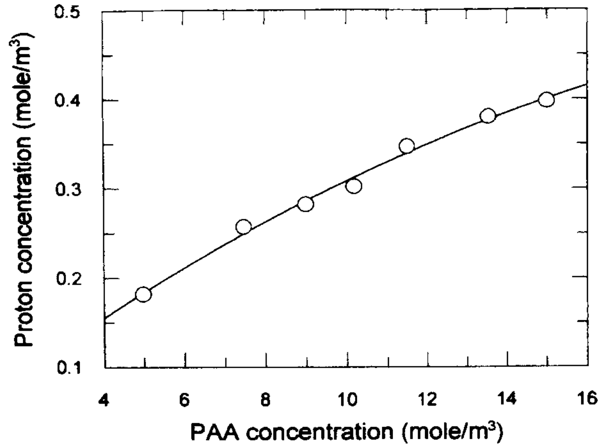

Fig. 1 Proton concentration of PAA/water system versus monomer concentration. The line represents a second degree polynomial function, $C_{H^+}(C_m) = a + bC_m + cC_m^2$, having the parameters: $a = 0.0280$, $b = 0.0344$ and $c = -0.0006$

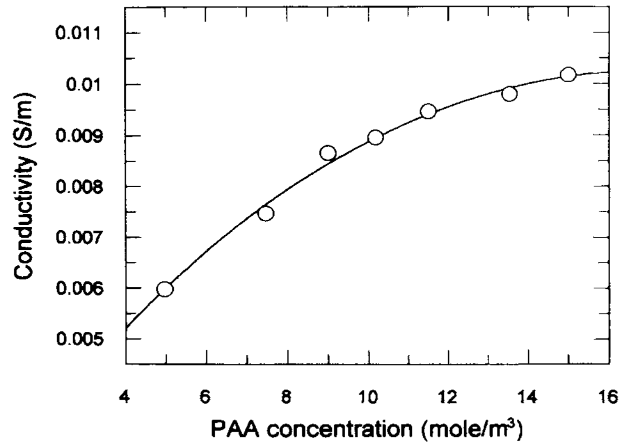

Fig. 2 Electrical conductivity of PAA/water system versus monomer concentration. Measuring frequency was 2.8 MHz. Solid line represents the theoretical simulation based on Eqs. (11), (12) and (13b). The best fit theoretical parameters were: $R = 22.2$ nm and $A = 0.40$. The polymerization degree of PAA was $g = 2100$, and the proton concentration was as expressed by the equation in the legend of Fig. 1

subsequent analysis of the conductivity data, the polynomial function was used instead of the measured proton concentration.

Figure 2 shows the measured conductivity of PAA/water system versus the molar monomer concentration. The full line represents the calculated values according to Eqs. (11), (12) and (13b), in which some considerations have been made. The hydrated volume of the polymer coil, V, was replaced by $4\pi/3R^3$, where R is the radius of the equivalent sphere. Also, the friction coefficient, r, was approximated with $r_0 = 6\pi\eta R$, where η is the viscosity of the continuum phase (water). The last approximation will result in some alterations of the final results. Nevertheless, replacing the radius of equivalent sphere with the hydrodynamic radius would introduce one more parameter into the theory (r/r_0) that is unlikely to be determined from conductivity measurements.

Taking into account all the above simplifications, the simulations of experimental conductivity data provided the values for the depolarization factor of the spheroid ($A = 0.40$) and the radius of equivalent sphere ($R =$ 22.2 nm). These results were further analyzed to find out more about the shape and dimensions of the PAA polymer coil. First of all, it can be observed that the value of 0.40 deduced for the depolarization factor corresponds to an oblate spheroid. The ratio of the spheroid semiaxes ($\alpha = 0.79$) was obtained by graphically resolving Eq. (5). Then, considering the equality between the oblate spheroid volume and the volume of the equivalent sphere (i.e., $ab^2 = R^3$), and using the calculated α value, the short and long semiaxes were computed. Accordingly, the two semiaxes values were: $a = 18.9$ nm and $b = 24.0$ nm. These values are in good agreement with the gyration radius of some 30 nm deduced from light scattering measurements [23].

As was specified in the theoretical section, the Eqs. (11) and (12) used in analyzing the conductivity data are approximate forms of the general theory. Therefore, it will be analyzed next whether the approximations made comply with the physical reality in the case of PAA/water systems investigated.

a) In deriving the expression for medium conductivity (Eq. (11)) the low frequency limit of Eq. (8′) was used, while the conductivity measurements were carried out at relatively high frequency. However, our measurements, made over a wide frequency range, revealed that no conductivity dispersion is present (see the experimental section), and this suggested that the measuring frequency was much smaller than the relaxation frequency of the system.

b) The mixture Eq. (12) was obtained by considering that the intrinsic conductivity of the polymer coil is negligibly small as compared to the external medium (i.e., $\sigma/\sigma_m \ll 1$). This assumption was verified by analyzing the data in Fig. 2 with the exact form of the Looyenga equation [9], instead of the more complicated equation of Boned and Peyrelasse (Eq. 2). The analysis (theoretical simulation not shown) provided a value of about 0.03 for σ/σ_m, and this well supported the approximation made in deriving Eq. (11).

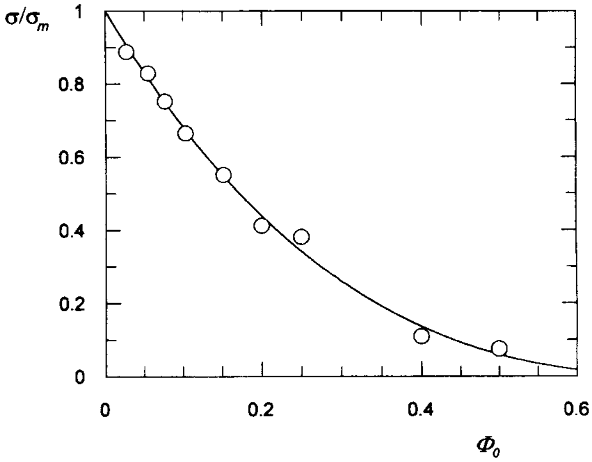

Fig. 3 Electrical conductivity of PEO ($Mw = 6000$) in 0.1 M KCl solution normalized to that of pure KCl solution (i.e., σ/σ_m). Experimental data, taken from ref. [2], were plotted against the dry volume fraction (Φ_0). Theoretical curve was computed from Eqs. (12) and (13a) by considering the hydration coefficient $h = 1.26$

Poly(ethylene oxide) in aqueous electrolyte solutions

As was mentioned above, the theoretical model is expected to apply, as a limiting case, to nonionic polymers in aqueous electrolyte solutions. In this case, the medium conductivity (see Eq. (12)) can be directly measured, prior to adding the polymer to the saline solution.

Bordi et al. [2] carried out electrical conductivity measurements on a series of PEO having different molecular weights, from 6×10^3 to 5×10^6. These authors demonstrated that the mixture equation of Looyenga much better simulates the measured conductivity than did the Maxwell–Wagner of Bruggeman equations. This finding was explained by considering that the polymer coils are not spherical, and their volume fraction in solution was very high.

We will next reexamine the data reported by Bordi et al. [2] by using the mixture equation of Peyrelasse and Boned [10]. Our purpose here is to demonstrate that, despite the very good agreement found by Bordi et al. between the Looyenga equation and experimental data, use of the equation of Peyrelasse and Boned provides more detailed information regarding the polymer coils. In our

Table 1 Geometrical characteristics of the PEO coil calculated for polymers with different molecular weights (see text for details)

Molecular weight	*a* (nm)	*b* (nm)
6×10^3	0.49	2.33
1.5×10^4	0.66	3.16
2×10^5	1.57	7.49
5×10^6	4.60	21.92

analysis, the approximate form of this mixture equation has been employed, namely Eq. (12). The volume fraction of the polymer was considered as defined by Eq. (13a).

Figure 3 shows the electrical conductivity of PEO (molecular weight 6×10^3) in aqueous electrolyte solution (0.1 M KCl) normalized to the conductivity of electrolyte solution alone. It is evident that the equation of Peyrelasse and Boned very well describes the data. According to this equation, the calculated hydration coefficient was $h = 1.26$, which compared very well with that reported by Bordi et al. ($h = 1.2$) [2].

In our reexamination of data, the depolarization factor was supplementarily obtained. This had a value of 0.75 (that is, an oblate spheroid), which provided an aspect ratio, α, of 0.21. Taking into account the equivalence between the two definitions of Φ (see Eqs. (13a) and (13b)), using the calculated values of h and α, and a partial specific volume of 0.885 cm^3/g for the dry PEO [2], the semiaxes values of the polymer coil were then calculated. These values were listed in Table 1 for different PEO molecular weights.

By comparing the data in Table 1 with the ones obtained for PAA/water systems, it can be readily seen that the semiaxes of the PAA coils are much larger for PAA than for PEO, even for higher molecular weights of PEO chains. This may happen because of the electrostatic repulsion appearing between the charged carboxyl groups of the same PAA chain, which renders an increased volume to the PAA coils.

Conclusions

The analysis of experimental data, in the light of the proposed theory, provided reliable structural information regarding both ionic and non-ionic polymers. It is to be noted that the theory may be applied to many types of colloidal systems, as for example to micellar solutions of ionic and non-ionic surfactants. However, some other phenomena, not included in the theory (e.g., the electrical double layer), may contribute to the measured conductivity. Therefore, care has to be taken when one is deciding which approximation is more suitable for the system investigated.

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