

Exploring the interactions in binary mixtures of polyelectrolytes: Influence of mixture composition, concentration, and temperature on counterion condensation

Ranjit De ^a, Hohjai Lee ^{a,*}, Bijan Das ^{b,*}

^a Department of Chemistry, Gwangju Institute of Science and Technology (GIST), Gwangju 61005, South Korea

^b Department of Chemistry, Presidency University, Kolkata 700 073, India

ARTICLE INFO

Article history:

Received 30 August 2017

Received in revised form 8 December 2017

Accepted 16 December 2017

Available online 18 December 2017

Keywords:

Electrical conductivity

Polyelectrolyte

Counterion condensation

Fraction of free counterions

Polyion transference number

ABSTRACT

The counterion condensation in the binary mixtures of like-charged polyelectrolytes with two different molecular weights, where both are negatively charged, has been studied by conductance measurement in aqueous medium. Sodium polystyrenesulfonate with two different chain lengths have been selected as model polyelectrolyte and the investigation has been carried out in the absence of any added salt. The specific conductance-polyelectrolyte concentration data were analyzed in the light of the scaling argument for the conformation of polyion chains in solutions to quantify the fractions of free counterions. Effects of polyelectrolyte concentration, molecular weights of the components of the mixture, and solution temperature on the condensation of counterions have been investigated to explore polyion-counterion interaction, and inter- and intra-chain interactions in these polyelectrolyte mixtures. This investigation revealed that the extent of counterion condensation is significantly influenced by the mixture composition, the polyelectrolyte concentration and the temperature. Evaluation of the polyion transference numbers provided important information as to the direction of the motion of the counterions under the action of the applied electric field.

© 2017 Published by Elsevier B.V.

1. Introduction

Polyelectrolytes are a special class of polymers with dissociable groups which ionize in polar media (e.g., water) to produce polyions and counterion bearing opposite charges. Owing to the strong electric field of the polyion, a certain proportion of the counterions becomes highly correlated with the polyion, i.e., a fraction of the counterions remains condensed onto the polyion chain. This phenomenon is known as the “counterion condensation”. Now, the extent of counterion condensation determines the charge on the polyion chains. It is obvious that the more the polyion charge, the stronger would be the intrachain electrostatic repulsion and hence there would be more stretching of the polyion chain. Thus both polyion charge and polyion size are governed by counterion condensation. Since polyelectrolytes present a ubiquitous class of materials and find widespread applications, a quantitative understanding of counterion condensation is of fundamental importance. While the behavior of counterion condensation in solutions containing single polyelectrolyte samples is now well-understood [1–6], the situation is far from satisfactory for multi-component polyelectrolyte solutions. Pairs of oppositely charged polyelectrolytes typically form complexes in aqueous solutions [2–6]. However, when both polyions have the

same charge, they exhibit electrostatic repulsion which could lead to phase separation caused by incompatibility. Although the former case has been extensively investigated in the field of interpolymer complexes [3–5], the later has been paid relatively little attention both from experimental and theoretical points of view. Various applications exhibit the tendency towards phase separation in solutions of similarly-charged polyelectrolytes, such as aqueous two-phase partitioning of biological molecules [4,5]. A complete characterization of such polyelectrolyte mixtures is, therefore, of utmost importance to understand the underlying mechanisms and/or molecular interactions governing the phase behavior for practical applications.

Studies exploring the interactions between the similarly-charged polyelectrolytes in a mixture are still in their infancy. Previous dynamic light scattering studies on aqueous binary mixtures of sodium polystyrenesulfonate with different molecular weights revealed coupled diffusion of polyions and counterions, which has been shown to be independent of the total polyelectrolyte concentration, mixture composition, and molecular weights of the two components [6]. Invariance of coupled diffusion of polyions and counterions implies an invariance of polyion-counterion interactions. Results from our previous conductometric studies, however, indicated a definite dependence of polyion-counterion interactions on both polyelectrolyte molecular weight and polyelectrolyte concentration in binary solutions [7–9]. These contradictory observations indicate that the nature of polyion-

* Corresponding authors.

E-mail addresses: hohjai@gist.ac.kr (H. Lee), bijan.chem@presiuniv.ac.in (B. Das).

counterion interactions in these systems in particular, and in polyelectrolyte mixtures, in general, is thus still unclear. In order to unravel the nature of these interactions in solutions, we have undertaken a study to probe various interactions occurring in these solutions using electrical conductivity measurement.

2. Theory

Colby et al. [8] put forward a theory for the electrical conductivity of semidilute solutions of polyelectrolytes without added salt using the scaling description for the configuration of a polyelectrolyte chain proposed by Dobrynin et al. [9].

In semidilute solutions, the polyion chain is modeled as a random walk of N_ξ correlation blobs of size ξ_0 , each of them containing g monomers. Each blob bears an electric charge $q_\xi = z_c e f g$ (z_c being the counterion valence, e is the electronic charge and f represents fraction of uncondensed counterions) and the complete chain, of contour length $L = N_\xi \xi_0$, bears a charge $Q_p = N_\xi q_\xi = z_c e f g N_\xi$. Due to the strong electrostatic interactions within each correlation blob, the chain is a fully extended conformation of g_e electrostatic blobs of size ξ_e . This means that for length scales less than ξ_0 , the electrostatic interactions dominate (and the chain is a fully extended conformation of electrostatic blobs of size ξ_e), and for length scales greater than ξ_0 , these interactions are screened and the chain is a random walk of correlation blobs of size ξ_0 .

Following this model, in absence of an added salt, the equivalent conductivity of a polyion in a semidilute solution is given by

$$\lambda_p = \frac{F z_c e f c \xi_0^2}{3 \pi \eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \quad (1)$$

where F is the Faraday constant, η_0 is the absolute viscosity of the solvent and c is the concentration of the polyelectrolyte solution expressed in the number of monovalently-charged groups per cm^3 .

In accordance with this model, Colby et al. [8] arrived at the following expression of the equivalent conductivity of a polyelectrolyte in a solution as a function of its concentration:

$$\Lambda = f \left[\lambda_c^0 + \frac{F z_c e f c \xi_0^2}{3 \pi \eta_0} \ln \left(\frac{\xi_0}{\xi_e} \right) \right] \quad (2)$$

where λ_c^0 is the limiting equivalent conductivity of the counterion.

This model treats the parameter f as an adjustable quantity which could be estimated from experiments in conjunction with this new approach.

3. Experiments

3.1. Materials

Two sodium polystyrenesulfonate (NaPSS) samples with molecular weights of $70,000 \text{ g mol}^{-1}$ (designated as P1) and $1,000,000 \text{ g mol}^{-1}$ (designated as P2) (each with a degree of substitution of 1) were procured from Aldrich Chemical Company, Inc. and were used without further purification. The chemical structure of NaPSS is shown in Fig. 1. The polymer samples were dried well for a prolonged period of time immediately prior to use for solution preparations. The puriss grade NaCl was purchased from Fluka and was well dried prior to use. To weigh the materials, a digital balance (Shimadzu) with weighing sensitivity of $\pm 0.2 \text{ mg}$ was used. Ultrapure water with specific conductance below $1 \mu\text{S cm}^{-1}$ at 298.15 K , used for the preparation of all solutions, was obtained from a Milli-Q (resistivity $18.2 \text{ M}\Omega \text{ cm}$ at 298.15 K) water purifying system. The uncertainty for the preparation of the sample solutions by dilution for investigations was assessed to be $\pm 0.2\%$.

NaPSS mixtures with different values of $x(P2) = c_p(P2) / (c_p(P1) + c_p(P2))$, where $c_p(P1)$ and $c_p(P2)$ are the concentrations of component 1 ($M = 70,000 \text{ g mol}^{-1}$) and component 2 ($M = 1,000,000 \text{ g mol}^{-1}$),

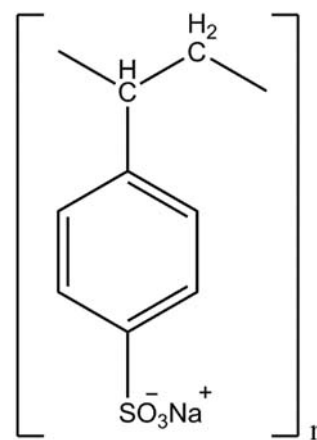


Fig. 1. Chemical structure of sodium polystyrenesulfonate. Molecular weight of each monomer unit is 206 g mol^{-1} .

respectively with c_p being the number of monovalently charged groups per liter *i.e.* equivalents per liter, were prepared. Total polymer concentration (c_p) was varied from 0.005 through $0.121 \text{ equiv L}^{-1}$, and mixtures with $x(P2)$ values of 0 (pure P1), 0.17 , 0.42 , 0.58 , 0.83 , and 1 (pure P2) were used for the present study.

3.2. Viscosity measurements

Viscosity measurements were carried out using a suspended level Ubbelohde viscometer kept vertically in a water thermostat which was placed on a vibration-free bench. The absolute viscosity (η) was obtained using the relation $\eta = (C\tau - \frac{K}{\tau})\rho$ where C and K are viscometer constants. The values of these constants were estimated to be $1.646 \times 10^{-5} \text{ cm}^2 \text{ s}^{-2}$ and -0.02331647 cm^2 , respectively, using the known density (ρ) and viscosity data of methanol and acetonitrile from the literatures [10,11]. The flow time (τ) was determined by using a digital stopwatch with capability of measuring time within $\pm 0.01 \text{ s}$. The combined expanded uncertainty in viscosity measurements was estimated to be $\pm 0.003 \text{ mPa s}$. The experimental temperature was maintained within $\pm 0.02 \text{ K}$.

3.3. Fourier transform-infrared (FT-IR) spectral measurements

The purity and complete sulfonation of these polyelectrolytes were confirmed via Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR spectra of both the NaPSS samples were recorded using an attenuated total reflectance (ATR) technique using a Jasco FTIR-4200 spectrometer with frequency resolution of 2 cm^{-1} ; the details of measurements are reported elsewhere [12]. Briefly, five characteristics peaks indicated by asterisk (*) symbol in Fig. 2, are observed at about 669 , 1010 , 1040 , 1128 and 1182 cm^{-1} ; these agreed well with the earlier literature values [13,14]. The peaks at 1010 and 1128 are assigned respectively to in-plane bending vibration of benzene ring and the in-plane skeleton vibration of benzene ring, whereas the peaks at 1040 and 1182 cm^{-1} can be assigned to the symmetric and antisymmetric vibration absorption peaks of SO_3^- group, respectively. The peak at 669 represents aromatic C—H out of plane bending (deformation) vibration [14]. Absence of peaks at around 699 and 759 cm^{-1} confirms complete sulfonation (degree of substitution of 1) of NaPSS as reported by the manufacturer. These two bands are to represent out-of-plane skeleton bending vibrations of benzene ring and out-of-plane bending vibration of the five —CH— groups in the benzene ring characteristic of monosubstituted benzene ring, respectively which are the characteristic bands of polystyrene samples [13].

Download English Version:

<https://daneshyari.com/en/article/7843273>

Download Persian Version:

<https://daneshyari.com/article/7843273>

[Daneshyari.com](https://daneshyari.com)