Colloids and Surfaces A: Physicochem. Eng. Aspects 343 (2009) 96–103

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Structure of poly (sodium 4-styrenesulfonate) (PSS) in electrolyte solutions: Theoretical modeling and measurements

Z. Adamczyk*, B. Jachimska, T. Jasiński, P. Warszyński, M. Wasilewska

Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Niezapominajek 8, 30-239 Cracow, Poland

ARTICLE INFO

Article history:
Received 30 September 2008
Received in revised form 5 January 2009
Accepted 30 January 2009
Available online 5 April 2009

Keywords:
Polyelectrolyte
Viscosity
Electrophoretic mobility
Conformation of polyelectrolyte

ABSTRACT

In this work, the structure of poly (sodium 4-styrenesulfonate) (PSS) molecules in electrolyte solutions obtained from theoretical simulations was compared with experimental data derived from dynamic light scattering (PCS), electrophoretic and dynamic viscosity measurements. Simulations and experiments were carried out for polymer having molecular weight of 15.8 kD and for various ionic strength of the supporting electrolyte (NaCl). It was predicted from molecular dynamic simulations that for the entire range of electrolyte concentration studied ($I = 10^{-3}$ to 0.15 M) the molecule behaved as a flexible rod. Its effective length L_{ef} varied from 12.5 to 8.5 nm, which corresponds to 0.79–0.56 of the contour length $L_{ext} = 16$ nm predicted for fully extended polymer chain. Thus, for electrolyte concentration of 0.15 M, a significant folding of the molecule was predicted, whose shape resembled a semi circle (torus). These predictions were compared with PCS measurements of the diffusion coefficient of the molecule, which allowed one to calculate its hydrodynamic radius R_H. It was found that R_H varied between 3.1 for $I = 5 \times 10^{-3}$ M and 4 nm for $I = 0.15$ M. These R_H values were in a good agreement with theoretical predictions stemming from Brenner's theory, approximating the true particle shape by prolate spheroids, bent to various forms. Using these R_H values and electrophoretic mobility data derived from microelectrophoresis, the average number of uncompensated (free) charges on the PSS molecule and the effective ionization degree were calculated. The number of free charges was determined to be 14–16 (decreasing slightly with ionic strength), which gives the ionization degree of 18–20%, which was comparable with theoretical predictions. Additional shape information was derived from the dynamic viscosity measurements of dilute PSS solutions using a capillary viscometer. The intrinsic viscosity derived from these measurements varied between 28.3 and 8 for the ionic strength 10^{-3} to 0.15 M. It was shown, after introducing the correction for hydration, that the experimental results were accounted well by the Brenner's viscosity theory for slender particle suspensions. The effective lengths derived from viscosity measurements using this theory was comparable with values predicted from the molecular dynamic simulations.

1. Introduction

Polyelectrolytes or polyions are molecules composed of a large number of covalently linked ionizable subunits. They are abundant in nature and essential for biological systems, just to mention DNA. Polyelectrolytes are often used in pharmaceutical, cosmetic and food industries, in ternary oil recovery, papermaking, for regulating rheological properties of suspensions.

Another important field of polyelectrolyte applications is preparing multilayer films on solid substrates of a desired composition and functionality [1–4], which is often realized by layer-by-layer (LbL) deposition of anionic and cationic polyelectrolytes. Such films can be used as convenient supports for proteins and nanoparticles, which can be easily embedded into the polymeric layer. A controlled formation of such polymeric films requires a throughout knowledge of the structure of macromolecules, their shape and charge in relation to its molecular weight, ionic strength and pH of solutions.

One of the efficient ways of learning about structural aspects of polyelectolytes is the rheological measurements, which have been performed extensively over the decades [5–8]. However, because of the variety of parameters influencing polyelectrolyte viscosity, these results are often misinterpreted using for example, the scaling theories of de Genes et al. [9], applicable for high molecular weight polyelectrolytes in solutions with no added salt only.

A better description of viscosity of polyelectrolytes in real solutions can be attained using the electrostatic wormlike chain theory developed by Odijk [10] and Skolnick and Fixman [11], known as the Odijk–Skolnick–Fixman (OSF) theory. This approach was based on the persistence length L_p concept, whose electrostatic contribution

---

* Corresponding author.
E-mail address: ncjachim@cyf-kr.edu.pl (Z. Adamczyk).

0927-7757/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2009.01.035

was calculated by solving the linearized Poisson–Boltzmann equation for a uniform line charge. It was predicted that because of electrostatic repulsion, this electrostatic component of L_p increases proportional to the square of Debye screening length κ^{-1},i.e., inversely proportionally to the ionic strength I of polyelectrolyte solution. The persistence length expression has been corrected by Davis and Russel [12] who calculated the correction valid for arbitrary κd_e (where d_e is the polymer chain diameter).

By exploiting the concept of the persistence length, Yamakawa and Fujii [13] formulated a viscosity theory for the wormlike polymers, which predicts that the intrinsic viscosity increases as $L_p^{3/2}$, i.e., proportionally to the cube of the Debye screening length. The OSF theory and Yamakawa–Fujii model was modified by Rushing and Hester [8], who proposed a semi-empirical model, which correlated the intrinsic viscosity of polyelectrolytes with its molecular weight and the screening length in the limit of high electrolyte concentration. They found, by analyzing extensively existing experimental data for various polyelectrolytes, that the slope of the intrinsic viscosity vs. screening length was 1.62 rather than 3.

The wormlike model was modified by Davis and Russel [12] who considered the excluded volume effect, which introduces additional stiffness of the polymer chain, characterized in terms of the chain expansion factor. This allowed them to renormalize the persistence length occurring in the Yamakawa–Fujii model and properly reflect the effect of the molecular weight and the ionic strength on the intrinsic viscosity for potassium poly (styrenesulfonate) solutions. Dobrynin et al. [14] proposed a necklace model of polyelectrolyte chain, in which its conformations were resulting from intrachain electrostatic interactions and counterion condensation on the polyelectrolyte backbone [15,16]. The necklace structure was obtained as a balance of the correlation-induced attraction of the condensed counterions and charged monomers and electrostatic repulsion between uncompensated charges. According to this model, the transitions of polymer conformations (chain-necklace-globule) depend on the value of the Bjerrum length determining the strength of the electrostatic interactions and the value of the Lennard–Jones interaction parameter, which controls the solvent quality for the polymer backbone.

The intrinsic viscosity data for the wormlike regime can be quantitatively interpreted in terms of the hydrodynamic model proposed originally by Kirkwood and Auer [17] who assumed an extended, rodlike shape of polyelectrolytes. In the more general case of ellipsoidal or spheroidal shape of macromolecules one can use the well-established results of Brenner [18] and Harding [19] who derived analytical solutions for the intrinsic viscosity as a function of the axis ratio. However, these theoretical results can only be applied if the shape of the molecule is known as a function of various physicochemical parameters.

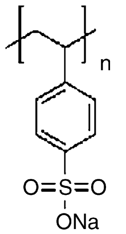
Therefore, a true structure of polyelectrolytes in solutions can only be unequivocally determined when exploiting complementary experimental data such as the hydrodynamic radius of molecules (containing shape information), their electrophoretic mobility, enabling estimations of the true ion condensation degree, etc. Additionally, the interpretation of experimental data can be facilitated by a comparison with theoretical simulations, based on the molecular dynamic approach, which furnish the necessary shape information.

Despite major significance of such a complete approach, there are few systematic works in the literature combining theoretical simulations of molecular structure with experimental measurements of diffusion coefficients and viscosity. In our previous work [20] such an approach was applied for determining polyacrylic acid (PAA) structure in aqueous solutions for various ionic strength and pH.

The goal of the present work is to determine theoretically and experimentally the structure of PSS molecules in electrolyte solutions, and the range of validity of the above viscosity theories. This anionic polyelectrolyte is widely used in basic studies [6–9,21], in drug delivery systems as the material for capsules' shells [22–23] and for charge regulation and stabilization of various suspensions.

2. Materials and methods

The polyelectrolyte used in our studies was the atactic poly (sodium 4-styrenesulfonate), hereafter referred to as PSS15, having the structural formula:



supplied by Polymer Standard Service GmbH, Germany. The averaged molecular weight M_w of the sample used in our experiments was 15.8 kD with the relative standard deviation less than 5%. The density in the condensed phase of the PSS sample was $\rho_e = 1.18 \times 10^3\ \mathrm{kg\,m^{-3}}$. Accordingly, the average volume of one

Table 1
Physicochemical characteristics of PSS15, $T = 293$ K.

Characteristic	Value, unit	Remarks
Density, ρ_p	1.18×10^{-3} kg· m^{-3}	Manufacturer
Molecular weight	15.8 kD	Manufacturer
Molecular weight of monomer	206 D	Calculated
Nnumber of monomers, nominal charges, N_m	77	Calculated
Bare chain diameter, d_e	1.1 nm	Calculated
Hydrated chain diameter d_h	1.39 nm	Calculated
Extended length, L_{ext}	16 nm	From simulations
Radius of gyriation, R_g	4.6 nm	Calculated
Equivalent sphere radius, R_s	1.54 nm	Calculated
Volume of molecule in crystalline state	22.3 nm^3	Calculated from specific density
Volume of extended bare molecule, v_c	15.2 nm^3	From simulations
Volume of hydrated molecule, v^*	24.3 nm^3	Calculated
Aspect ratio of bare molecule $\lambda = L_{ext}/d_e$	14.5	Calculated
Aspect ratio of hydrated molecule, $\lambda^* = L_{ext}/d_h$	11.5	Calculated
Hydrodynamic radius of bare molecule (extended cylinder), R_H^*	2.5 nm	Calculated from Brenner's theory
Hydrodynamic radius of hydrated molecule (extended cylinder), R_H	2.64	Calculated from Brenner's theory
Intrinsic viscosity of bare molecule (extended cylinder) $[\eta]$	23.8	Calculated from Brenner's theory
Intrinsic viscosity of hydrated molecule (extended), $[\eta]_c$	17	Calculated from Brenner's theory
Number of uncompensated charges per molecule N_c	21–23	From simulations