

MODELING OF THE PARTICLE SCATTERING STRUCTURE FACTOR FOR BRANCHED BIO-POLYMERS IN SOLUTION: A X-RAY SCATTERING STUDY

PIETRO CALANDRA,^a MIKHAIL A. KISELEV,^b AND DOMENICO LOMBARDO^{a*}

ABSTRACT. We present a study which illustrates the modeling of the Particle Scattering Structure Factor from Small Angle X-ray Scattering (SAXS) data. The studied sample was a poly(amidoamine) Pamam dendrimers in water solution. The intra-particle form factor $P(q)$ has been analyzed employing an inverse Fourier transformation which allows to obtain the particle pair distance distribution function and to gain information about dendrimer shape. The experimental inter-dendrimer structure factor $S(q)$ has been analysed in the framework of liquid integral equation theory for charged systems in solution. From that, we derive an effective interparticle interaction composed of a screened Coulombic plus hard-sphere repulsion potential, which allow the estimation of the dendrimer effective surface charge Z_{eff} . The present analysis, applied to a Pamam dendrimers in water solution, strongly supports the finding that structures and interaction of dendrimer is strongly influenced by charge effects. As a result, this quantity can be considered as a crucial parameters for the modulation of the degree of structural organization in solution, suitable for a number of potential applications.

1. Introduction

The interaction of electromagnetic radiation with particles represents a fundamental way to approach a variety of spectroscopic techniques. The relevant response function of these particles varies strongly with several parameters, such as their size, shape and environmental conditions, thus requiring significant characterization efforts in order to gain a deeper insight into the physics governing their structural and dynamic behavior[1]. Among the electromagnetic scattering techniques, Small angle X-ray scattering (SAXS) represents a powerful technique for nanoparticle description in a very broad resolution range (from nanometer to micrometer) which provides unique information on the nanostructure and kinetics at the boundaries of many disciplines in the field of science and technology [2].

In this study we describe the modelling of the scattering particle form factor in a water solution of a Polyamidoamine (Pamam) dendrimer, a highly branched biopolymers of interest in the field of biotechnology and material science [3, 4]. Moreover the experimental inter-dendrimers structure factor $S(q)$, obtained from the X-ray Scattering data, was analyzed in the framework of the Ornstein-Zernike integral equation [5]. The performed analysis strongly supports the findings that the effective intra- and interdendrimer charge

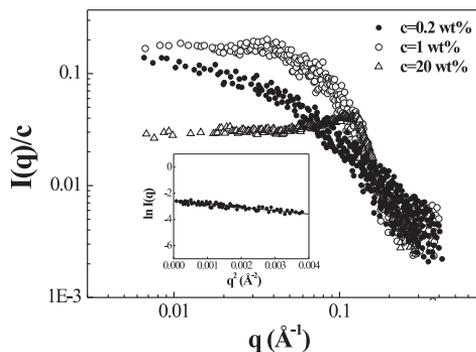


Figure 1. SAXS profiles of water solution of G=1.5 Pamam dendrimers for three different concentrations (C=0.2 wt% circles, C=1 wt% open circles, C=20 wt% open triangles).

interactions, as well as the dendrimer solution environment conditions, are crucial parameters for the modulation of the degree of structural organization in solution, suitable for a number of potential applications [5, 6].

2. Materials and Methods

Pamam dendrimers of generation $g=4$ ($M_w=14215 \text{ g mol}^{-1}$) were purchased from Sigma-Aldrich. The investigated system consists of a tetrafunctional ethylenediamine core and $[-\text{CH}_2\text{CH}_2(\text{C}=\text{O})\text{NHCH}_2\text{CH}_2\text{N}<]$ spacers and is terminated at the final generation with 64 amine terminal groups (NH_2) in average.

Small Angle X-ray scattering measurements were carried out at the D22 SAXS station of the LURE DCI synchrotron radiation facility (Orsay). The chosen angular range provided data from $q=0.005 \text{ \AA}^{-1}$ to $q=0.5 \text{ \AA}^{-1}$ (q is the scattering vector equal to $4\pi\sin\theta/\lambda$, θ is half of the scattering angle, and λ is the X-ray wavelength). The scattering intensities $I(q)$ from the samples, detected by a gas-type linear detector, were corrected for the incident beam decay, sample thickness, and transmission.

3. Results and Discussion

In order to obtain valuable information about the structure and interaction of our investigated system a set of SAXS measurements has been carried at the polymer concentrations of C=0.2 wt% C=1 wt% and C=20 wt% (Fig. 1).

In the dilute region the interparticle interaction can be neglected (i.e., $S(q)\sim 1$), so that the analysis of scattering intensity $I(q)$ can furnish direct information on morphological features of the scattering particles. In that case the SAXS intensity $I(q)$ can be expressed as a function of the scattering wavevector q and the dendrimer radius of gyration R_g by mean of the following expression: $I(q)=I(0)\exp(-q^2R_g^2/3)$ [2]. The analysis on the slope of $\ln I(q)$ vs q^2 in the so called Guinier region (i.e. for $qR_g \ll 1$) for the concentration of

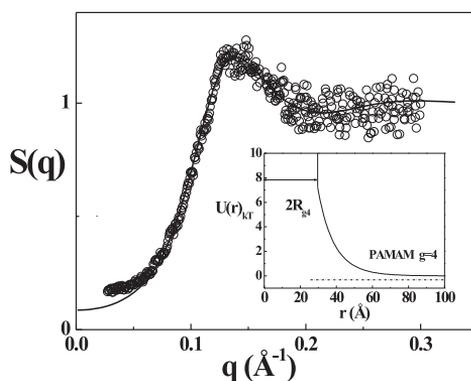


Figure 2. Comparison between the experimental and the computed (by means of the HNCA scheme) structure factor $S(q)$ for polymer concentrations of $C=20$ wt%. In the inset a schematic representation of the effective inter-dendrimers interaction, composed of a screened Coulombic plus hard-sphere repulsion potential, is presented.

$C=0.2$ wt% furnishes an average value of $R_g=19.0$ Å for the dendrimer radius of gyration (inset of figure 1).

In order to obtain information about the inter-dendrimer interaction potential the charged dendrimers can be approximated as impenetrable spheres of radius R whose charge Ze is distributed on the surface. Those spheres are immersed in the uniform neutralising background of the solvent molecules which participates with its dielectric constant and which produces also a screening effect in the system. According to this model the repulsive potential between two identical spherical objects (macroions) of diameter $\sigma=2R$ placed at a distance r (centre to centre distance) is given by [7, 8]:

$$U(r) = \frac{Z_0 e^2}{4\pi\epsilon(1 + \kappa\sigma)^2} \frac{e^{-\kappa(r-\sigma)}}{r} \quad (1)$$

Here κ is the Debye-Huckel inverse screening length which is determined, at a given temperature T , by the ionic strength I of the solvent (in mol/l) [7]. Moreover an hard sphere type repulsive component for the potential has been adopted to represent the close contact inter-dendrimer interaction as schematically shown in the inset of figure 2. According this model we have investigated the observed inter-dendrimer structure factors $S(q)$, obtained by SAXS experiments, by means of the solution of the Ornstein-Zernike equation [8].

According to this schemes the equilibrium structural properties of a macroion solution are computed by numerical methods starting from the knowledge of some structural parameters, such as the particles concentration (in mol/l), the effective charge in Ze and the particle diameter D . More specifically, while the particle concentration and diameter are fixed values, the effective charge Ze has been assumed to vary in order to fit the experimental $S(q)$. In our specific case we have investigated the observed inter-dendrimer structure

factors $S(q)$, obtained by SAXS experiments, in terms of the hypernetted chain approximation scheme (HNCA) [8]. The structure factor for a system of interacting particles can be written as

$$S(q) = 1 + \int_0^\infty 4\pi^2 \rho_C [g(r) - 1] \frac{\sin(qr)}{(qr)} dr \quad (2)$$

where $\rho_C = c/M$ is the particle number density (number of particles per unit volume). In fig. 2 the numerical structure factor $S(q)$ computed according the HNCA scheme [8] has been compared with the experimental structure factor obtained from SAXS spectra at the dendrimer concentration of 20%. From the figure it is clear how the adopted model reproduces quite satisfactorily the experimental results with the same average dendrimer effective charge of $Z_{eff} = 10.5 \pm 0.5$ (in unit of electron charge $|e|$), corresponding to a degree of ionisation which is around 16%. A rather different result has been obtained in a SAXS investigation in water solution of half integer Pamam generation $g=3.5$ containing COO-Na surface endgroups [6]. In that case, in fact, analysis coming from SAXS experiments revealed a dendrimer effective charge of $Z_{eff} = 24e$ (i.e. a degree of ionization near 40%), which is attributed to a stronger dissociation of the sodium carboxilate (COONa) surface groups in aqueous media. This circumstance confirms that that most structural and interaction properties of starburst dendrimers in solution are regulated by the electrostatic nature of the interactions of the dendrimer chargeable moieties with the solvent molecules.

4. Conclusions

We present the modeling of the scattering structure factor in highly branched biopolymers in solution. The analysis of the experimental inter-dendrimer structure factor $S(q)$ in the framework of the Ornstein-Zernike integral equation, allows us to adopt a suitable model for the charged dendrimer systems in solution. More specifically the modeling of the inter-dendrimer interaction potential in terms of a screened coulomb potential allows us to obtain important information about the dendrimer effective charge Z_{eff} (degree of ionisation). The obtained results point out the important role of the dendrimer charge in regulating, through the modulation of the electrostatic interaction, main part of their structural properties in solution. It can be concluded that the development of appropriate models for the description of the main spectral features in scattering experiments results in a suitable interpretation of the molecular conformation as well as furnishing important information about the interaction of (nano-)particles in solution in the field of soft condensed matter.

References

- [1] F. Volino, Spectroscopic Methods for the Study of Local Dynamics in Polyatomic Fluids. In: J. Dupuy and A.J. Dianoux, Editors, NATO ASI-series B, Plenum Press, New York (1978).
- [2] Glatter O.; Kratky O. Small-Angle X-ray Scattering; Academic Press: London, 1982.
- [3] Tomalia D. A.; Naylor A. M.; Goddard W. A. Angew. Chem. Int. Ed. Engl. 1990, 29, 138-175.
- [4] P. Calandra, C. Giordano, A. Longo, V. Turco Liveri, Materials Chemistry and Physics 98 (2006) 494-499.
- [5] L. Bonaccorsi, D. Lombardo, A. Longo, E. Proverbio and A. Triolo, Macromolecules 42 (2009), 1239-1243.
- [6] D. Lombardo, Langmuir 25 (2009), 3271-3275.
- [7] Hunter R. J. Foundations of Colloid Science; Oxford University Press: New York, 1986; Vols. I-II.
- [8] Hansen J. P. and Mc Donald I. A. Theory of Simple Liquids; Academic Press, New-York, 1986.

^a CNR-IPCF, Istituto per i Processi Chimico-Fisici
Viale F. Stagno D'Alcontres, 37
I-98158, Messina, Italy

^b FLNP, Joint Institute for Nuclear Research
Joliot-Curie 6
Dubna, I-141980, Russia

* To whom correspondence should be addressed | Email: lombardo@me.cnr.it

Paper presented at the ELS XIII Conference (Taormina, Italy, 2011), held under the APP patronage; published online 15 September 2011.

© 2011 by the Author(s); licensee *Accademia Peloritana dei Pericolanti*, Messina, Italy. This article is an open access article, licensed under a [Creative Commons Attribution 3.0 Unported License](#).