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Electro-optic properties of organic nanotubes

Stoyl P. Stoylov [a,*], Svetla Stoilova-McPhie [b]

[a] Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria
[b] University of Texas Medical Branch at Galveston, USA

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ABSTRACT

In this review article the theoretical and experimental possibilities of applying EO-methods for estimation of the physico-chemical properties of the organic nanotubes (ONTs) are studied. The ONTs are highly organized nanostructures of strongly elongated, anysometric, and hollow cylinders with a size range of 1 nm to 10,000 nm, e.g. in aqueous solutions they could behave as colloid (disperse) particles. They have high interaction ability due to their extremely large curved, rolled-up external surfaces (bilayers of membrane walls) and unique properties because of their specific electric charge distribution and dynamics that make possible the functionalization of their surfaces. Thus they could template guestsubstances such as membrane proteins and protein complexes on the exterior surfaces and in the membrane. We performed our investigations for the case of ONT aqueous colloid suspension. Following our earlier proposition of the general expression for the electro-optic (EO) effect we derived equations for the evaluation of the electric properties of ONT particles such as mechanism of electric polarization and identification of their most important electric Dipole Moments (DM), permanent (pDM) and induced (iDMs). Further we recommend ways for the calculation of their magnitude and direction. Also we evaluated some geometrical properties such as length of the ONT particles and their polydispersity.

The knowledge that we provided about the ONT properties may enable us to elucidate and predict their biological activity. Templating biological active ligands (such as membrane proteins and protein complexes) on the inner and outer surfaces as well as in the surface membrane creates their potential usefulness as carrier and deliverer of biopharmaceuticals in bio-nanodevices.

The theoretical equations were compared with the experimental data for ONTs such as (lipid) LNT, Tobacco Mosaic Virus (TMV) and microtubules (MT). Comparison of EO methods with other methods used till now shows that the EO methods are faster, not invasive and do not alter the studied particles.

Contents

* Corresponding author. Tel.: +359 878444586; fax: +359 29712688.
E-mail address: stoylov@yahoo.com (S.P. Stoylov).

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1. Introduction

Organic nanotubes (ONTs) are self-assembled, highly organized supramolecular structures of hollow cylinders with size in the nm to μm range. They have highly curved surfaces and specific electric charge distribution and dynamics. These properties are responsible for their significant interaction ability upon functionalization of their surfaces to incorporate or/and attach guests substances through interactions to their inner and outer surfaces [1–4].

Since the ONT size ranges from 1 nm to 10,000 nm, they could be regarded as strongly elongated, anisotropic colloid particles and therefore susceptible to be investigated with the methods of Colloid Electro Optics [5]. The ONT's electro-optic (EO) properties [5–22] defined by EO methods depend directly on their geometrical, electrical and optical properties, as well as on the polydispersity of the system. ONTs in aqueous media could be regarded as a suspension, whose properties as a system depend on its dispersity, i.e. changes in the particles' interfaces are directly related to changes in the particles dimensions.

In general EO methods are based on the investigation of the optical response of the systems to the applied Electric Field (EF). The most studied EO phenomena are electric light scattering, electric birefringence and electric dichroism.

Unlike the dielectric properties (electric permittivity and conductivity) [24], the EO properties are a source of valuable information not only about the mechanism of electric polarization of the particles but also about their size and polydispersity. The EO properties depend only on the reorganization of the electric charges in the suspension related to the orientation of the particles. All other mechanisms of electric charges distribution are related directly to the dielectric properties of the particles and not to the EO properties of the suspensions. Thus, while the EO properties of a suspension depend directly on the electric properties of single colloid particles, the dielectric properties reflect the electric properties of the whole colloid suspension.

The emphasis in this paper is on the most studied and important dipole moments (DMs): the permanent (pDM) and induced (iDM) dipole moments. Our goal is to propose a robust algorithm for the investigations of colloidal systems, capable to determine the type, magnitude and direction of their DMs through measuring the changes of the EO effect of the colloidal system in the Hz, kHz and MHz frequency ranges of the applied EF [22]. In this review we consider the application of the EO theory to the study of some important physico-chemical properties of ONT. Some corrections and additions to the general EO theory are considered that could be useful for the theoretical analysis of ONT and other colloid particles. The parts of the EO theory, which do not show essential changes when applied to ONT, have not been discussed.

In this review we discuss the advantages of the EO methods for studying organized supramolecular structures in the 1 to 10,000 nm range. These methods are not invasive, as their application doesn't deform or destruct the ONT's organization. They are fast and highly sensitive to the electric properties not only of the particles but to the system as a whole, which can give invaluable information on the macromolecular organization and function of complex biological structures. Other well established biophysical and structural methods such as Circular Dichroism, Electron Microscopy (EM), Atomic Force Microscopy (AFM) and X-ray crystallography are much slower and experimentally demanding techniques, which can be complemented significantly with the EO studies.

In this paper we propose electro-optically derived equations for the identification of the mechanism of polarization, which are directly related to the type of the iiDM of different ONT, as well as the equations for determination of the magnitude of the DMs and the length of the particles. Based on the EO theory we also discuss one of the methods for evaluating the polydispersity of ONT suspensions, as well as the determination of the directions of the DMs with respect to the longest ONT axis.

There are various types of ONTs [4]. In this review we illustrate the specific applications of the EO theory with experimental studies for both synthetic ONT, as lipid bilayer nanotubes (LNT) and naturally occurring ONT as Tobacco Mosaic Virus (TMV) and microtubules (MT). These novel (for the LNT) and already published (for MT and TMV) experimental data further prove the reliability of the recommended EO methods.

2. EO effect of a disperse system — theoretical remarks

The investigations of the electro-optic (EO) properties of colloid suspensions of ONT in this review are based on the "Orientational theory" [5]. The main assumption is that the EO-effects are due only to the particles' orientation upon the application of the electric field (EF). Other possible mechanisms such as particles' deformation and aggregation are neglected [5]. Changes in the order of the system could be followed through the EO response to the changes of the EF parameters such as: frequency (ν), EF strength (E) and the duration time (t) of the EF. Theoretical equations corresponding to the experimentally defined ν-, E- and t-dependences of the EO effects were proposed for the determination of the mechanism (type) of polarization, magnitude and direction of the ONT's electric dipoles, as well as length and polydispersity of the ONT particles.

2.1. Time (t) dependence of the EO-effect (G^t)

In general, AC rectangular electric pulses are applied to the colloid suspensions in the EO experiments. Switching on the EF orients the particles and the EO-effect (G^r) rise until the steady-state region (G^{st}). After switching off the EF, the particles disorient and the EO-effect decays (G^d), (Fig. 1) [5]. From Fig. 1 it is possible to measure the values of G^t at a given time after switching off the EF. The experimentally obtained values for G can be entered in the theoretical equations (see Eqs. (1) to (21)) for the determination of some electrical and geometrical properties of the ONT particles.

2.2. Frequency (ν) dependence of the EO-effect (G^ν)

The ν-dependence of the EO-effect is also called dispersion dependence (DD). The DD may be composed of several dispersion curves. DD may be defined as the change in the magnitude of the EO-effect with the change in the frequency of the applied EF. The DD reflects the rearrangement of the electric charges following (pDM) or causing the alignment (iiDM) of the ONT particles, which cannot follow the frequency changes of the direction of the EF. The DD ends when this process cannot follow at all the changes of the direction of the electric field with the frequency. In Fig. 2 an idealized example of one dispersion curve (EO-effect vs. ν) is given. The magnitude of a dipole moment is determined from the amplitude (M) and its type-from the frequency at which the amplitude is halved (M/2) (ν_{cr} of the dispersion and of the particles).

For different types of dipole moments, ν_{cr} are different, which gives the possibility to experimentally determine the type of the dipole moment. In Fig. 3 the DD is presented with three different idealized dispersion curves. In Fig. 3 a DD with three different idealized dispersion curves (Dispersions) is presented.

The frequency range of the EO measurements should be several (or better several tens) MHz where the EO-effect has measurable magnitude