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Observation of sol–gel transition for carbon nanotubes using electroacoustics: Colloid vibration current versus streaming vibration current

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Abstract

Propagation of ultrasound through a porous body generates an electric signal, similarly to the well-known electroacoustic effect in dispersions of mobile particles. This obscure version of electroacoustics has been known since 1948, when M. Williams published his paper on electrokinetic transducers [M. Williams, Rev. Sci. Instrum. 19 (10) (1948) 640–646]. We observe this effect in a 1 wt% aqueous dispersion of carbon nanotubes. Magnitude and phase of the electroacoustic signal, as well as conductivity, are sensitive to sonication and mixing. Sonication with no mixing leads to phase rotation by up to 180° comparing to the traditional colloid vibration current (CVI) in sols. This is explained by the fact that sonication terminates motion of the carbon nanotubes by building up a continuous network gel. Propagation of ultrasound through the immobile carbon nanotube network generates a streaming vibration current (SVI), but not a CVI, which requires free motion of the particles relative to the liquid. Theoretical analysis indicates that the SVI has 180° difference in phase from the CVI. The magnitude of the SVI after sonication with no mixing depends on the shifts of the measuring probe position. Apparently this occurs due to inhomogeneity of the carbon nanotube gel, which might have clusters with higher density and gaps with no solids at all. This effect can be used for testing homogeneity of the carbon nanotube gel. Sonication with continuous mixing also affects the electroacoustic signal and conductivity. However, the electroacoustic phase does not reach 360°, which corresponds to the SVI in gel. The measured signal is the vector sum of the CVI and SVI under these conditions. It is possible to use data on the electroacoustic phase to monitoring the number of carbon nanotube segments that retain independent motion.

Keywords: Streaming current; Colloid vibration current; Sol–gel transition; Carbon nanotubes

1. Introduction

We observed the effect that is described in this paper accidentally. One of the potential users of our electroacoustic ζ-potential probe DT-300 asked us to verify the applicability of this instrument for characterizing carbon nanotubes. The results were very surprising and forced us to look at the literature. It turned out that similar effects had been observed much earlier. The earliest relevant work that we found was published by Williams in 1948 [1]. It was experimental, but with useful and completely forgotten industrial application. Theoretical model was developed about 30 years later [2]. There has been no follow-up for the past 30 years. We consider the observed effect quite useful, because it opens up a new way of characterizing porous bodies. The scope of electroacoustic ζ-potential probes can be expanded substantially by including porous bodies for characterization of their electric surface properties.

This paper presents results of our more detailed investigation that followed up our initial findings.

Our customer provided us with dry carbon nanotubes. We prepared aqueous dispersions at 1 wt% and performed a set of measurements using various schemes of sample handling. In the original setup we inserted the probe into the beaker with the sample, which could be either immobile or mixed with a magnetic mixer. In the later setup we used the sample chamber of our instrument DT-1200, which allowed mounting electroacoustic and conductivity probes in the walls and pumping the sample through.

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Results of the measurements turned out to be very sensitive to the sample handling. This is unusual. Normal stable dispersions exhibit practically the same electroacoustic signal independent of the method of the probe mounting, unless sedimentation does not affect stability. This is clearly not the case with structured carbon nanotubes dispersion. Electroacoustic measurement apparently is quite sensitive to the structure, and can even be used for monitoring the homogeneity of the structure. Illustration of this statement is one of this paper's purposes.

However, the most surprising discovery was the behavior of the electroacoustic phase. It corresponded to a positive surface charge of the carbon nanotubes, whereas independent tests indicated that they are negatively charged. To explain the meaning of this contradiction, we present electroacoustic measurements in some detail.

We measure the electroacoustic signal as an alternating current at a frequency of 3 MHz. This current comes as a result of ultrasound propagation through the system. It was shown 70 years ago by Debye that propagation of ultrasound through a liquid that contains charged species, ions or colloid particles, generates an electric response [3]. In the case of colloidal particles this is called colloid vibration current (CVI).

This signal, like all alternating signals, can be characterized by magnitude and phase. The magnitude of CVI depends on the volume fraction, the ζ-potential of the dispersed phase, and some other parameters. A detailed theory is given in the book [5].

The phase of CVI reflects first of all the sign of the particles' surface charge. There is a convention relating CVI phase with ζ-potential sign. Positive ζ-potential yields CVI phase values around 360°, whereas negative ζ-potentials are associated with CVI phases around 180°. Theory predicts that increasing particle size might affect CVI phase as well, but no more than 45°.

We have consistently measured the electroacoustic phase of sonicated immobile structured carbon nanotube dispersions as 360° with a few degrees variation. According to the well-known, well-tested, and widely accepted electroacoustic theory, this points toward positively charged particles.

However, microelectrophoretic measurement tells us unambiguously that carbon nanotubes are negatively charged in 0.001 M KCl solution, such as we prepared the dispersion in.

Existing electroacoustic theory does not know any effect that would alter electroacoustic phase by 180°, other than the sign of the surface charge. This means that existing electroacoustic theory cannot explain our experimental data for carbon nanotubes. We have been forced to look for a new electroacoustic theory.

We found the first clue when measuring stirred samples. There has also been a phase shift, but not as big as 180°. The phase was in the range of 250°–320°. Mixing destroys the carbon nanotube network. This points toward this structure as a reason for the phase shift.

It is possible that carbon nanotubes linked into the network become completely immobile and even ultrasound cannot move or shake them.

Existing electroacoustic theory assumes that ultrasound moves particles relative to the liquid due to the density contrast. This assumption might be not valid for structured carbon nanotube dispersions. Ultrasound would still go through the structured network, but carbon nanotube segments would not move relative to the laboratory frame of references

This does not mean yet that termination of the carbon nanotubes' motion would eliminate relative motion of the liquid. The gradient of the pressure in the ultrasound wave would move the liquid relative to the immobile carbon nanotubes. It would squeeze the liquid as in the case of a membrane. This motion would drag ions of the carbon nanotubes' double layer. This motion of ions would be registered by our probe as an electroacoustic signal.

This situation is well known in classical colloid science [6]. Electric current generated by a gradient of pressure is called streaming current.

We are coming to the conclusion that ultrasound can generate a streaming current when it propagates through the network of immobile carbon nanotubes. We suggest calling it a streaming vibration current (SVI) to reflecting that it is alternating with a frequency identical to the ultrasound frequency. Similar effect had been predicted and observed many years ago for membranes [1,2,5].

A simple analysis presented below in Appendix A indicates that the phase of the SVI is 180° reversed from the phase of the CVI.

Our experimental data presented below can be interpreted as a result of transition from CVI to SVI. Structuring of carbon nanotubes causes this transition. It can be controlled by application of ultrasound and/or mixing.

When the measured phase is 360°, the measured signal is only SVI. When the measured phase is much below 360°, measured signal is a vector sum of the CVI and SVI.

At the end we suggest several potential applications of this effect.

2. Materials

We use carbon nanotubes produced by Jeio Co., Ltd., Seoul, Korea and received through our supplier.

A dispersion is prepared as 1 wt% of these carbon nanotubes in a 0.001 M KCl aqueous solution. This and other potassium chloride (KCl) solutions are prepared using powder produced by J.T. Baker Chemical Co.

For chemical modification of the carbon nanotubes we use sodium hexametaphosphate from Fluka, UK.

For calibrating the electroacoustic probe we use silica Ludox TM-50 produced by Grace–Davison and purchased from Sigma–Aldrich. The original dispersion contains 50 wt% silica. We dilute it down to 10 wt% using a 0.01 M KCl solution. Silica has ζ-potential -38 mV in this solution.

Calibration of the conductivity probe has been done using distilled water and two KCl solutions with concentrations 0.01 and 0.1 mol/l.

3. Experimental techniques

We used an instrument manufactured by Dispersion Technology Inc., Model DT-300. It has electroacoustic sensors as