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Characterization of the structure of ultra dilute sols with remarkable biological properties

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Abstract

Most natural waters are probably "ultra dilute": aquasols. While the composition of such waters is routinely characterized thoroughly with respect to composition, very little attention has been paid to the solid phases which are certainly suspended in most, if not all, such. Our recent work having established the importance of the structure of water on its properties, [[1]; R. Roy, W.A. Tiller, I. Bell, M.R. Hoover; Mater Res Innov. 9 (2005) 577.] we have examined the structures of many waters with easily demonstrated (e.g. silver aquasols) or long-claimed (e.g. homeopathic remedies) biological effects. The results show that such materials can be easily distinguished from the pure solvent, and from each other, by the use of UV–VIS and Raman spectroscopy, while FTIR is insensitive to these differences. This opens up a whole new field of endeavor for inorganic materials scientists interested in biological effects.
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1. Introduction

Sols have a significant role in materials science. In 1956, one of the authors, Roy[b] wrote a review paper [2] describing his development of a new process for making ultra pure, ultra fine ceramics. It was the birth of the "sol–gel" process. (also Ref [3]) which, after 3–4 decades became the standard route for fine ceramic synthesis used in some 50,000 papers. The second generation 1987 review of the field by Roy [3] includes the development of di-phasic aquasols (i.e. mixed nano-solids in the same liquid, water) as the route to ultrahomogeous nanocomposites. A relevant finding from this work is the remarkable phenomenon of *solid state epitaxy* where one solid phase–usually crystalline–can serve as a template and impart its structure to the amorphous *solid* phase to 'force' the amorphous phase to crystallize in the crystalline structure of the template [4–8]. Could solids suspended in water also impart structure to the liquid phase? This might explain what has proven to be an extremely intriguing problem, i.e. the surprising health effects of ultra-dilute sols, especially those involving metallic solids, containing say, 1–10 atom ppm of the suspended solids.

Textbooks on the phase rule and thermodynamics have always been unclear on the key question: "Is say a 0.1 to 1% sol of clay in water, one phase or two?" In other words, does the sol have a unique structure? This question becomes very relevant in explaining the biological activities of such materials. Recently there has been a flurry of patents and papers on the anti-microbial properties of metal aquasols with concentration in the range of 1 atom ppm. [9]. Our own detailed work of Ag-aquasols is an example of a thorough characterization of such materials [10]. Colloids, specifically, including metallic sols, have been studied by more of the greatest scientists over decades than any other similar category of materials. In his most cited paper on Brownian motion in 1905, Einstein is [11] apocryphally reported to have commented that a "colloid acts

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like an atom," implying, presumably, some "structuring" of the water by the presence of the charged solid phase.

Ultra dilute sols (containing ~ ppm solids) [12] have very surprising biological properties. (Table 1 in Ref [10]). Is the presence of the silver (or other active ingredient in the solvent) changing the structure of the water—as a single phase in the phase rule sense? These are the questions we answer empirically herein. Along a similar line, we undertook in the present research to study a group of other ultradilute sols of both inorganic and organic solutes, which have for 200 years claimed remarkable biological activity. The present study targets only structural changes in both dilute and ultra dilute aquasols and alcosols employing primarily spectroscopic analytical tool to evaluate possible significant structural changes.

2. Experimental

This paper is only a note on some of these interesting new findings. A much longer paper has been submitted elsewhere on part of this work, to which the reader is referred for more details both on the experimental and the larger pattern of results [13].

3. Materials studied

Specific silver aquasols manufactured by a unique high voltage (100,000 V) process of electrolysis across silver electrodes in pure water [14] received much of our attention, although several others were examined.

In addition to such aquasols, which show biological activity down to near 1 ppb, it occurred to us that we could answer a question, which has engaged the medical world for nearly 200 years. The world of modern medicine (and derivatively modern science) reject the very concept of homeopathy on the argument that since all the solute atoms have been diluted beyond the Avogadro limit, the homeopathic remedy *can be no different from the pure solvent, and can therefore have no biological activity.* There is, of course, a massive flaw in this argument used by generations of *chemists*, since the key paradigm of *materials science* (as distinct from solution chemistry) states "Structure (most significantly), not composition, controls properties". Graphite and diamond, interconvertible in milliseconds in our laboratory, are chemically identical while being (nearly) the softest and very hardest of materials. This work merely addresses the question: Is the structure of such an ultradilute sol identical with the original solvent?

4. Techniques

We have used SEM, TEM, E-TEM and cryo-TEM to study the solid phases present in the metal aquasols. For the bulk "liquid sol" we have used UV–VIS, FTIR, and Raman spectroscopy both in the metal aquasols and ultradilute sols. UV–VIS spectroscopy and Raman spectroscopy proved to be useful tools to investigate the subtle but significant changes in the structural parameters in both dilute and ultradilute aqua/alcosols. While other techniques such as freezing point depression; acoustic loss spectroscopy, ellipsometry, viscosity, surface tension, have been explored and will eventually be used in depth to measure entirely different properties, we report here our experience with the major spectroscopic techniques which are widely available. Although UV–VIS and Raman data are very much a function of the machine and the technique, our analyses were repeated several times to confirm the reproducibility of the data. Details on the experimental techniques are published elsewhere [13].

5. Results

Nature of the solid phase in Ag-aquasol. Five different specimens of colloidal silver nanoparticles (from different suppliers) were evaluated by TEM to identify the nanostructure of the particles and the possible phases comprising the nanoparticles. (Refer to Ref [10] for experimental details). Fig. 1(a, b) illustrates TEM images of two different colloidal silver specimens. Note the size of the silver particles range from several nanometers (nm) up to ~100 nm. Specifically, the shape and size of the nanoparticles in sample (b) are more uniform compared with those from sample (a). Fig. 1(c) is a high-resolution image of one nanoparticle, where the lattice planes are clearly defined. It demonstrates that the nanoparticles are largely crystalline, and not in the amorphous form. To identify the possible phases, electron nanodiffraction was utilized. In this diffraction mode, a small parallel electron beam allows one to obtain the diffraction pattern from the small specimen area. Fig. 1(d) shows one (among several dozen) typical electron nanodiffraction pattern from these colloidal silver specimens. What one can conclude is that these particles are largely, highly crystalline metallic silver.

Nature of the "liquid phase" in Ag-Aquasol. The "liquid phase" in Ag-Aquasol has been thoroughly investigated using Raman spectroscopy and UV–VIS spectroscopy. The well-known bond-stretching absorptions are shown in Fig. 2a for silver colloidal samples with 10, 32, 200 ppm of Ag in distilled water. While the main O–H stretch peaks do not show much variation with the Ag concentration, the change in

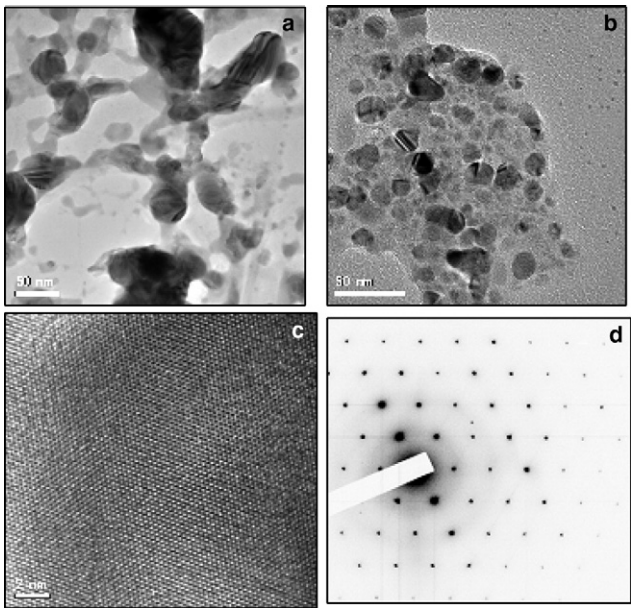

Fig. 1. (a, b) TEM images of the two different colloidal silver specimens. (c): High-resolution electron microscopy image of a Ag nanoparticle (d) Electron nanodiffraction pattern from Ag nanoparticle.

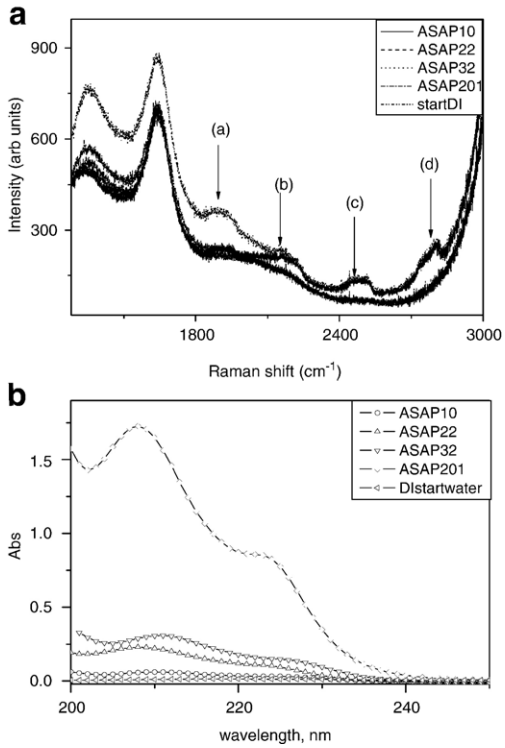

Fig. 2. a: Raman spectra of Ag colloidal samples. Structural differences in the ultradilute colloids are identified as peaks (a–d). b: UV–VIS spectra of silver colloidal samples showing an increase in absorption maximum with Ag concentration.

position of the peaks identified as (a)–(d) clearly indicate the existence of structural changes in silver aquasols. The position, relative intensity and shapes of the peaks in both stretching and bending modes are again remarkably similar. It is far too early to assign such changes to particular effects. This is further confirmed by the absorption spectra shown in Fig. 2b. The UV-absorption spectra of aqueous silver nanoparticles shows only one symmetric absorption peak at ca. 420 nm, which is the characteristic surface Plasmon resonance of spherical silver nanoparticles [15]. However, in our Ag-aquasols, we DO NOT observe any characteristic absorption peak at 420 nm, instead we observe a sharp absorption at ca. 208 nm and another absorption peak at ca. 222 nm. While subtle changes in the particle morphology induce distinct spectral responses [16], we note that the observed absorption maxima in our samples increase as a function of the Ag concentration thus implying significant structural changes in the solvent.

Following our detailed work in Ref [1], it appears possible therefore, that both UV–VIS and Raman Spectroscopy could serve as simple and useful tools for identifying the differences between the pure solvent and the ultra dilute sols prepared by other processes: sequential dilution and succussing. In this regard, fully cognizant of many scientists' reaction to the term 'homeopathy', but remaining only dedicated to the data, we have studied two ultradilute alcosols (so-called homeopathic remedies) to identify any possible structural changes in the solvent. *Nearly 200 runs* have been made to calibrate every step in the experimental configurations and procedures used for the different instruments.

Ultra dilute sols containing active ingredients in concentrations beyond a dilution of 1 in 10^{24} (24 X or 12C), wherein, not even a single molecule of the starting material is likely to be present, are considered for the present study. Two sets of analyses are presented for remedies prepared by standard homeopathic techniques as procured from Hahnemann Laboratories: *Nat Mur* and *Nux Vomica*. It may be noted that both Nat Mur and Nux Vomica are prepared in 95% ethanol and henceforth will be referred to as alcosols. For comparison, specific homeopathic remedies with different potencies [Nat Mur 6C, 12C, 30C, and Nux Vomica 6C, 12C, 30C] are shown in Fig. 3. Each dilution involves vigorous shaking, a process called 'succussion', (see Ref [1]),

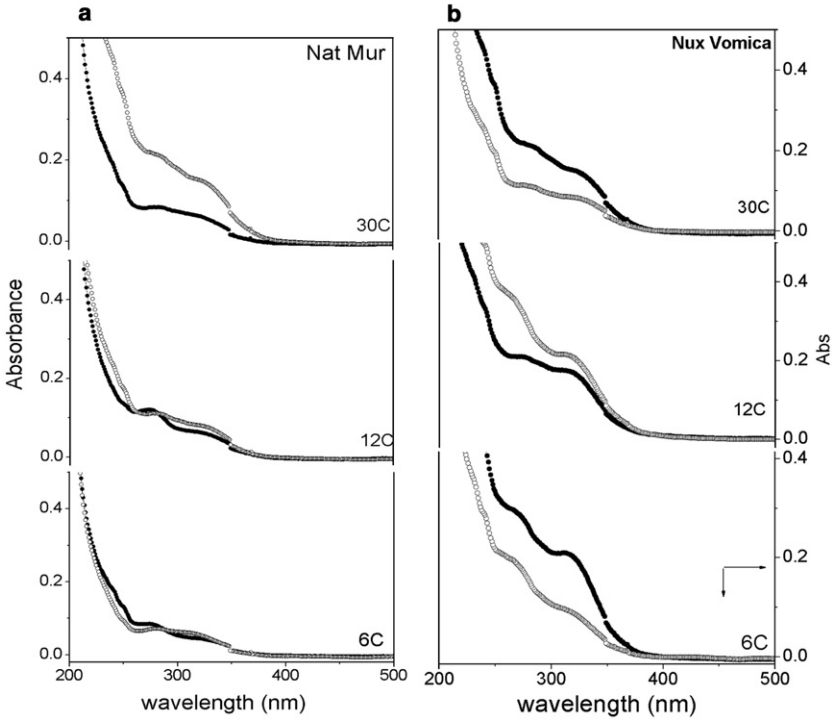

Fig. 3. The two curves shown for the six families in 3(a) and 3(b) represent the envelope spectra within a series of 10 duplicate preparations of each remedy.

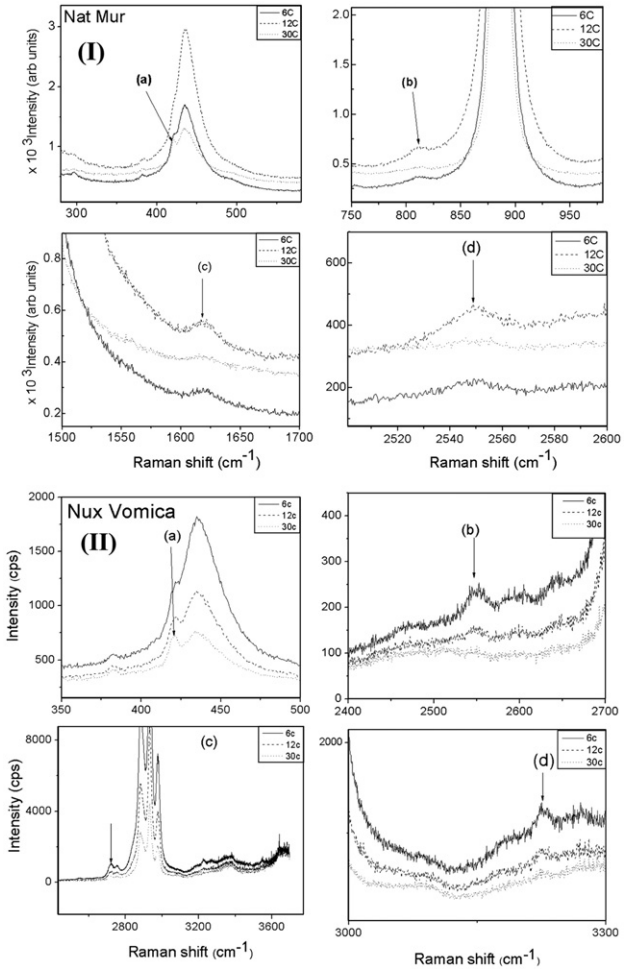

Fig. 4. Raman spectra of 6C, 12C and 30C of Nat Mur and Nux Vomica remedies showing structural differences in peaks identified as (a–d) in 4(I) and 4 (II).

which 'potentizes' the diluent molecules. So absence of *any* starting solute in preparations more dilute than 24X or 12C is accepted.

In our calibration studies, the UV–VIS absorption spectra for the ultra dilute remedies showed an envelope of differences within a series of 10 separate duplicate preparations of each remedy of Nat Mur and Nux Vomica. The spectra of the different groups, however, show clear differences between

(a) The two different remedies
(b) Different potencies of the same remedy for both Nat Mur and Nux Vomica.

Fig. 3 shows side by side comparisons of two different solutes ("remedies"). Fig. 3a compares the same solute at different levels of dilution and succussion.

The data condensed here make 2 points:

1. The "solute content" of the aquasol (Nat Mur or Nux Vomica) definitely makes a difference in the spectra. Compare in Fig. 3a — 30C with 3b— 30C; likewise for 12C and 6C.
2. Within each solute family, i.e. within Fig. 3a or separately 3b, the dilution and succession levels (6C, 12C and 30C) also clearly affect the spectra.

This appears to indicate the existence of significant structural changes in the solvent under these ultra dilution conditions. This is further supported by Raman analyses shown in Fig. 4(I). A clear distinction in the Raman — active modes is noted between the two different remedies as well as among the different potencies of the same remedy. The peak identified as (a) has a shoulder in the 30C that is absent in the 6C and 12C potencies; peaks (b)–(d) are more prominent in 12C than in the other potencies, similar peak variations around the bending mode are noted in Nux vomica alcosol as shown in Fig. 4(II).

6. Conclusions

From this preliminary study, it is rather clear that even an ultradilute sol is indeed structurally different from the pure liquid solvent phase. The data on the ultradilute sols prepared with succussion, show clear differences between the differently treated samples. This suggests that whether due to epitaxial effects, effects from the "pressure, 2nd phases, or nanobubbles caused by the succussion, the differences are *real*. Our preliminary analytical study, which certainly requires confirmation, clearly throws insight on the key question "Does a sol represent a one or two-phase system?" Further work is underway to conclusively draw a line, but it would suggest that such sols may indeed be a "one phase" system.

Acknowledgements

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