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Raman spectroscopy of magnetoliposomes

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Abstract

In this study Raman spectroscopy was used to investigate monolayer and bilayer magnetite-based magnetoliposomes (MLs). The Raman probe is the hydroxyl (OH) group chemisorbed at the magnetite nanoparticle surface. Measurements were performed at room temperature in the typical OH stretching region. The data gathered for both samples are compared to each other and with those obtained for pure water. In comparison to liquid water (2.74 kcal/mol), it was found that the hydrogen bond strength between the chemisorbed OH-group and the polar headgroup of the inner phospholipid layer was reduced in both the monolayer (2.22 kcal/mol) and the bilayer (1.83 kcal/mol) ML samples.

Keywords: Interface structure; Light scattering; Magnetoliposomes; Spectroscopy—optical

1. Introduction

Magnetoliposomes (MLs) are biocompatible, physiologically stable structures, consisting of a phospholipid-based vesicle filled with nanosized magnetic particles [1]. Innovative applications of these structures deal with, for instance, oral drug-delivery systems [2] and magnetic resonance imaging markers for cancer diagnosis [3]. In this study Raman spectroscopy is proposed as a valuable experimental technique to investigate the interaction between the chemically active nanoparticle surface and the polar headgroup of the inner layer phospholipids.

Similarly to the strategy used to investigate ionic and surfactant-stabilized magnetic fluid (MF) samples [4–7], the Raman probe used in our investigation is the OH-stretching mode associated to the hydroxyl-group chemisorbed at the nanoparticle surface. Liquid water is used as the model picture. It shows five OH-stretching modes in the 3000–4000 cm^{-1} region, arising from various amounts of hydrogen bonding [8]. The two OH-stretching Raman modes in the higher end frequency of the spectra (ν^s and ν^a) describe non-hydrogen bonded (OH...) modes. ν^s is a symmetric while ν^a is an anti-symmetric OH-stretching mode. In contrast, the three Raman components (ν_d^s, ν_d^a and ν_b) at lower frequencies describe hydrogen-bonded (OH....) modes. ν_d^s, ν_d^a refer to symmetrically OH.... modes, while ν_b refers to the anti-symmetric OH.... mode [8,9].

2. Experimental

Preparation of MLs used in this investigation followed a three major step procedure. A laurate-coated magnetite-based MF sample was prepared in the first step. In the second step, the magnetite-coated MF sample was incubated with preformed phospholipid vesicles, while in the third step, the resulting biocolloid was submitted to a dialysis process in the presence of preformed vesicles. After the third step, magnetic nanoparticles enveloped with either a monolayer or a bilayer of phospholipids were obtained. The samples had a particle concentration of 3×10^{15} and 4×10^{15} particles/cm^3. Details of the whole preparation procedure were described earlier [10,11]. Both ML samples (monolayer and bilayer) were used to take the room temperature Raman spectra. The Raman setup consists

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of a double 0.85 m 1401 Spex monochromator equipped with the usual photocounting system. The 514 nm line from an Argon ion laser, at an optical power of the order of 150 mW, was used to illuminate the ML samples.

3. Results and discussion

Fig. 1 shows a schematic representation of the interface nanoparticle surface-phospholipid layer in (a) the bilayer ML and (b) the monolayer ML. In particular, Fig. 1 highlights one configuration in which one oxygen anion of the phospholipid polar headgroup may bind to the surface oxy-metal ion (Me^{n+}–O–P) while the other oxygen anion of the same polar headgroup establishes a hydrogen bonding with the OH-group chemisorbed at the nanoparticle surface (OH....O–P). There may also be phospholipid polar headgroups linked to the oxy-metal ion at the nanoparticle surface without establishing hydrogen bonding with the surface OH-group. It could also be possible that some to the phospholipid molecules in the inner layer of the bilayer ML establishes only hydrogen bonding with the surface OH-group. When the outer shell of the double phospholipid layer is removed, as schematically represented in Fig. 1(b), some of the phospholipid molecules may face the polar headgroup towards the aqueous medium, thus favoring colloidal stability of the monolayer ML in the polar medium.

Fig. 2 shows the typical Raman spectrum of water as well as the Raman spectra of both monolayer ML and bilayer ML. While five (two symmetric, two asymmetric, and one full hydrogen bonding) OH-stretching Raman modes were identified in water, only the two asymmetric Raman modes were observed in the monolayer and bilayer MLs. The fitting procedure (gaussian) identifies the anti-symmetric hydrogen-bonded mode (ν_b) plus the anti-symmetric non-hydrogen bonded one (ν^a). The quenching of the three modes (two symmetric and one full hydrogen bonding) in the Raman spectra of the ML samples testify that the Raman features are dominated by the OH-groups chemisorbed at the magnetite surface [7]. Indeed, while in water the OH-stretching modes ν_b and ν^a peak at 3399 and 3628 cm^{-1}, respectively, the corresponding values for the monolayer ML are located at 3634 and 3684 cm^{-1}, and for the bilayer ML at 3644 and 3691 cm^{-1}. Note that a shift (with respect to the corresponding modes in water) in the $\nu_b(\nu^a)$ Raman mode of about 235 (56) and 245 (63) cm^{-1} was observed in the monolayer and bilayer ML samples, respectively.

Finally, the relative area under the curve of the ν_b and ν^a modes depends on the ML type investigated. The fitting procedure indicates reduction of the population ratio ν_b/ν^a to about half, when one moves from the bilayer to the monolayer ML sample. This change in the population ratio (OH..../OH...) can be explained considering the removal of the outer phospholipid layer from the bilayer ML to produce the monolayer ML sample. Upon removing the outer phospholipid layer from the bilayer ML sample, some of the phospholipid molecules belonging to the inner phospholipid layer

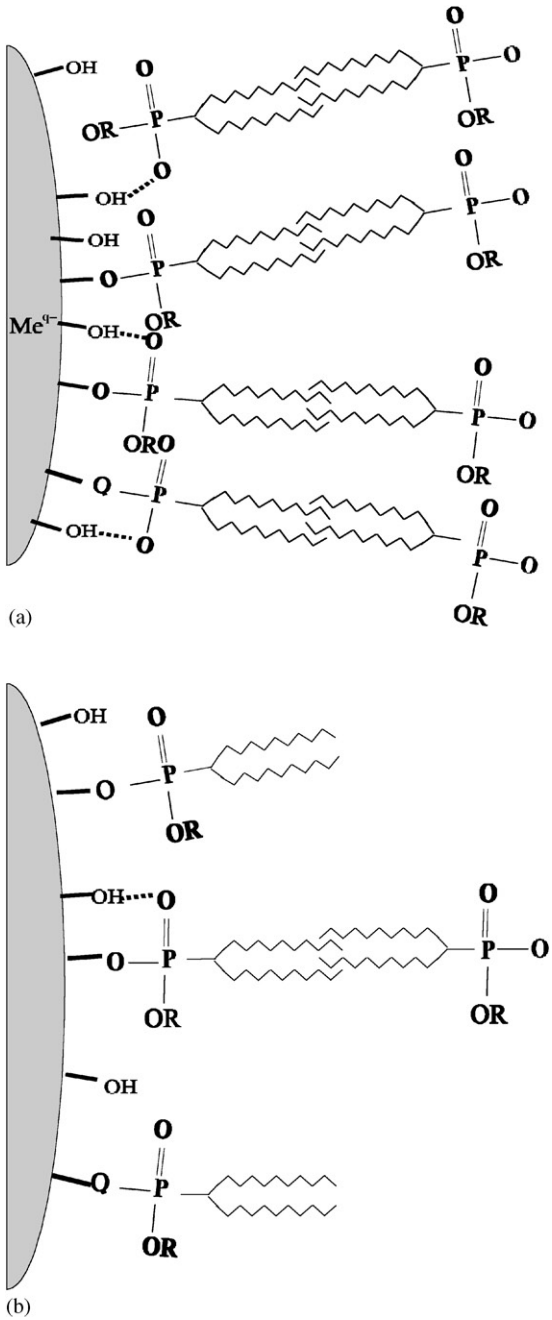

Fig. 1. Schematic representation of the interaction between the nanoparticle surface and the phospholipid layer in (a) the bilayer ML and (b) the monolayer ML.

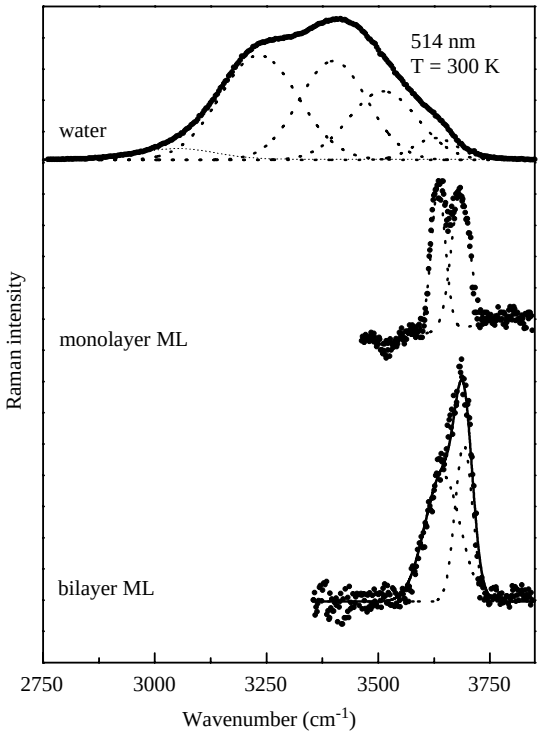

Fig. 2. Raman spectra of water, monolayer ML and bilayer ML in the OH stretching region. Dashed lines represent the best numerical fit using gaussian-shaped modes.

originally facing the polar headgroups towards the nanoparticle surface may reorganize themselves in order to face the polar medium. Such reorganization of the phospholipid layer may explain the reduction of the population ratio ν_b/ν^a in the monolayer ML in comparison to that found for the bilayer ML. It is possible to use the ν_b/ν^a ratio to estimate the hydrogen bonding strength between the surface OH-group and the oxygen atom present in the polar headgroup. Details of the calculation of the hydrogen bonding strength based on the ν_b/ν^a ratio can be found in Ref. [4]. We find that the estimated hydrogen bonding strength is larger for the monolayer ML sample (2.22 kcal/mol) than for the bilayer ML sample (1.83 kcal/mol), indicating that the OH-bond in the monolayer ML sample is stronger than that in the bilayer ML sample.

4. Conclusions

In summary, Raman spectroscopy would be used as a powerful technique to investigate the microscopic details of the interaction between the inner phospholipid layer surrounding the nanoparticle surface and the nanoparticle surface itself. Similarly to surfactant-stabilized MF samples the quenching of the symmetric OH stretching modes from the Raman spectra of the ML samples indicates that chemisorbed OH-groups at the magnetite surface dominate the light scattering process. The reduction of the hydrogen bonding strength observed in the ML samples with respect to the liquid water indicates a weaker interaction between the OH-group at the nanoparticle surface and the polar headgroups from the phospholipid layer. Such interaction is weaker in the bilayer ML than in the monolayer ML sample.

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