Coenzyme Q Induced Modifications in Heterogeneous Systems of Biological Significance

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The 'Proton-motive Q Cycle' proposed by Mitchell [1] requires the CoQ acting as electron and proton carrier through the membrane and the membrane 'fluid' enough to allow the interaction between the coenzyme and the redox sites. To elucidate this point we studied the effects of the CoQ and his homologues on the liposomes and on the inside-up vesicles of lecithin (EPC) used as membrane models.

It has been shown that the length of the polysoprenoid side-chain does not affect the chemical properties of the quinonoid head and that the phenyl side-chain is less flexible than the hydrocarbon chains of the membrane phospholipids [2]. Nevertheless, ESR and fluorescence show that the short-chain CoQ homologues reduce the fluidity of the system, while the long-chain homologues enhance the fluidity [3]. Moreover, the freeze-etching electron microscopy indicates that the CoQ dissolved in phospholipidic vesicles makes more fluid the less fluid states but immobilizes the lipid bilayer in the more fluid states.

^{31}P-NMR in liposomes indicates that the quinonoid moiety of the CoQ and his homologues interacts with the phosphatidic groups directly or by means of the associated water molecules, while ^{13}C-NMR fails to show interactions on the CoQ and his homologues either with the choline groups or with the fatty acid residues. ^{2}H-NMR relaxation time (T_1) measurements on $^{2}H_2O$ in liposomes suspensions show that the length of the side-chain plays an important role in the exchange of the water between the interior and the exterior of the vesicles. Proton relaxation times (T_1 and T_2) measurements carried out in inverted vesicular systems prove that two water populations exist in these model systems and that long-chain CoQ homologues modify the organisation of the water populations and their distributions, while no effects, or very little, are observed for the short-chain homologues.

A possible explanation of the reported observations is that ESR, fluorescence and EM, rather than variations in the fluidity of the lipidic components of the vesicles, reflect the effects of the water behaviour modified by the different CoQ homologues dispersed in the model systems.

In fact the CoQ and its long-chain homologues have the side chain long enough to span entirely the bilayer arrangements making a sort of channel for the water exchange.

References

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The Water–Protein Interaction as Detected by Nuclear Relaxation Studies

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The frequency dependence of the longitudinal relaxation rate (T_1^{-1}) of the water protons in protein solution [1, 2] makes it unequivocally evident that water senses the overall motion of the protein molecule. The observed relaxation rates can be related to the rotational and translational mobility of the water molecules only if the relaxation mechanism of water protons occurs independently of the relaxation of protein protons.

The existence of a strong magnetization transfer (cross-relaxation) between the two spin populations has been inferred [3–5] in various protein–water systems from either the effect of the isotopic dilution with D_2O or the behaviour of the free induction decay.

The T_1^{-1} measurement is normally carried out by using strong π and $\pi/2$ rf pulses which uniformly affect all the protons in the sample (non-selective excitation). In this case the rate constant is [6]:

$$R_1\,(\text{non-selective}) = R + \sum_S \left(\sigma_{IS}\frac{\gamma_S}{\gamma_I}\right)$$

where R is the total direct relaxation rate and σ_{IS} is the cross relaxation term between spin I and S. Alternatively, the I spins may be excited with a relatively weak rf pulse while the S resonances remain essentially unperturbed (selective excitation). In this case the initial rate R_0 of the non-exponential recovery may be defined as: