Mg(II) Adsorption to a Phosphatidylglycerol Model Membrane Studied by Atomic Absorption and FT-IR Spectroscopy

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A study was undertaken of the interaction of the Mg ion, i.e., Mg(II), with the anionic phosphatidylglycerol (PG), one of the five lipid species present in the thylakoid membrane of plant chloroplasts. The number of Mg(II) binding sites (n_0) in PG bilayer vesicles (PGV) was determined by equilibrium dialysis and atomic absorption spectroscopy, and the Mg(II) binding sites were identified by Fourier transform infrared (FT-IR) spectroscopy. The coordination interactions of the Mg ion in the phosphorylglyceryl moiety of PG were then examined in the framework of the lattice created by intermingling PG molecules. The FT-IR study shows that the sites of Mg(II) coordination are the negative charge in PO_2^-, the C−O−P−O−C and C−O−C residues, and the *sn*1 and *sn*2 ester C═O's, as was also observed in bilayer membranes constituted of digalactolipids (Fragata, M.; Menikh, A.; Robert, S. *J. Phys. Chem.* **1993**, *97*, 13920). A major finding is that $n_0 = 8.1$, meaning that Mg(II) binds or coordinates to about eight PG molecules. This result is particularly interesting, since it is directly related to the coordination number (CN) 8 of the Mg ion in a crystal lattice. CN = 8 is thus a clear indication that the metal ion−lipid array adopts a Mg(II)−8PG lattice or molecular arrangement. An important question in this respect is the determination of the lattice energy per PG mole, U_0/PG, and the Born's energy of charging a Mg ion, $\Delta\mu$, that is the change in free energy on transferring Mg(II) from a medium of low dielectric constant (ϵ), i.e., the H_2O−PG interface ($\epsilon \approx 25-32$), into one of high dielectric constant, i.e., the bulk aqueous solvent ($\epsilon \approx 78$). The calculations show that $\Delta\mu$ is between −27 and −18 kJ mol^{-1} and U_0/PG = 129 kJ mol^{-1}. That is, $\Delta\mu$ is considerably smaller than U_0/PG. A straightforward conclusion is that the diffusion of the Mg ions from the H_2O−PG interface into the bulk aqueous phase is energetically favored but might not occur. This therefore means that the calculations are consistent with the experimental observation that extensive dialysis of the PGV membranes cannot extrude the bound Mg ions out of the PG head group. In conclusion, the Mg(II)−8PG lattice concept developed in the present work is a new molecular or fractal set, e.g., a Mandelbrot set, that will be instrumental in modeling the structures and geometries that minimize the opposing forces responsible for the stability of the lipid bilayer membrane (see, for example, Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 1973).

1. Introduction

The interaction of the Mg ion, i.e., Mg(II), with phosphatidylglycerol (PG), an anionic lipid of the thylakoid membrane of plant chloroplasts, is essential to the function of photosystem II (PSII) (see, for example, refs 1 and 2). Although the participation of PG in various photosynthetic processes has been made the object of a large number of studies (see, for example, refs 1−5), the nature of its interaction with Mg(II) and the PSII proteins still awaits to be resolved in enough detail and refinement to generate a structural model with mechanistic significance. In this respect, it was shown that PG is a constituent of the PSII core complex where its relative content is about 4 mol/mol PSII reaction center, i.e., P680.[6] A fundamental aspect of the question is the observation of Siegenthaler and Mayor[4] that the conformation of the D1 protein in the PSII core complex is affected by the loss of phosphatidylglycerol. The visualization of this effect is clearly depicted in a recent model discussed by Kruse and Schmid[5] showing that phosphatidylglycerol is required to maintain the D1 protein conformation that sustains the activity of the PSII units. In Kruse and Schmid's model[5] the binding site of PG is in a groove that appears to be located between arginine 27 and arginine 225 (Sayre et al.[7]). The D1 protein would be thus inactive in the absence of PG, since the functional conformation of the polypeptide is dependent on the presence of the phospholipid (cf. Figure 7 of ref 5). Moreover, the incorporation of the PG molecules into the D1 protein may yet be conceived as a step toward their interaction with more specific components of the PSII complex such as the Mn cluster (see Figure 5 of ref 8) or the aromatic amino acid residues and the photosynthetic pigments, i.e., the P680 chlorophylls and pheophytin, in the PSII reaction center (see Figure 1 of ref 9). An interesting working hypothesis in the framework of the molecular models discussed so far[5,8,9] is to assume that the enhancement by Mg(II) of the PG-mediated stimulation of oxygen evolution in PSII[2] results from a rearrangement of the phospolipids lattice.

In this paper we used PG bilayer vesicles (PGV) as a model membrane in the context of an investigation of the structure−function relationships between Mg(II) and the lipid constituents of the thylakoid membrane. First, the number of binding sites of Mg(II) in PGV was determined by equilibrium dialysis and atomic absorption spectroscopy. Second, the binding sites of Mg(II) in PGV were identified by Fourier transform infrared

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(FT-IR) spectroscopy. Then the coordination interactions of the Mg ion[10] in the low-polarity pocket in the phosphorylglycerol moiety of the intermingling PG molecules were examined in the context of the lattice created by the oxygens in C−O−C and the phosphate group, and the *sn*1 and *sn*2 ester C═O's.[11]

2. Experimental Section

Chemicals. L-α-phosphatidylglycerol was purchased from Serdary Research Laboratory (London, Ontario). $MgCl_2$ (Sigma Chemical Co., St. Louis, MO) was purified as described in Lessard and Fragata.[12] All other compounds were obtained from Sigma Chemical Co. and Pharmacia Fine Chemicals AB (Uppsala).

Fatty Acid Analyses. The analysis of the fatty acid chains was performed by gas chromatography of methyl esters formed from methanolysis of the lipid (0.1 mg) with 1 mL of BF_3/MeOH 14% wt/vol (Pierce Chemical Co.). The mixture was heated 15 min at 100 °C followed by cooling for about 10 min. Then *n*-hexane and distilled water were added to separate the fatty acid methyl esters, which were dried by treatment with anhydrous Na_2SO_4 followed by a current of nitrogen. The residue was dissolved in 50 mL of *n*-hexane. The fatty acid analysis was carried out in a Varian gas chromatograph, Model 3700, equipped with a Shimadzu integrator, Model C-R3A, using nitrogen as the carrier gas. The determined fatty acid chains composition in mol % (in parentheses) is 16:0 (36.45), 16:1 (0.63), 18:0 (12.67), 18:1 (32.59), 18:2 (11.6), and 18:3 (2.97).

Preparation of PG Vesicles. The phosphatidylglycerol vesicles were prepared according to methods described previously.[13] The dried lipid at a concentration of 10 mg mL^{-1} was dispersed in 0.01 M Tris-HCl buffer (pH 8.0), then vortexed in a refrigerated capped tube fixed in a cup−horn installed in a Model W-225R sonifier cell disrupter, Heat Systems-Ultrasonics (Plainview, LI). The output power was set at 160 W. The cup−horn system was used to avoid metal contamination of the lipid dispersion with the titanium particles from the sonifier probe. The samples were sonified for about 13−15 min, that is, till the dispersions became clear.[13b] The efficiency of the sonication procedure was verified for each preparation by molecular sieve chromatography on a Sepharose-4B gel (Pharmacia Fine Chemicals AB, Uppsala) column.

Determination of the Adsorbed Ligand Concentration. The binding of Mg(II) to the phospholipid bilayers was obtained by incubating aliquots of the cation solutions with a known volume of vesicles suspended in 0.1 M NaCl and 0.01 M Tris-HCl buffer (pH 8.0) to give the final desired concentration of $MgCl_2$. The vesicles solutions were then dialyzed against several changes of 0.01 M Tris-HCl buffer (pH 8.0), which did not contain NaCl. The dialysis time was evaluated as the time required to totally deplete of salts a dialysis bag (Spectra-Por no. 1) containing the Mg ions at concentrations identical with those present in the lipid-containing bags. At the end of the dialysis period the cation content of the lipid membranes (bound ligand concentration) was determined by atomic absorption spectroscopy with a Perkin-Elmer, Model AA-1278 apparatus, and the lipid content was evaluated by phosphate analysis using a modified procedure of Bartlett.[13a,14] The important point here is that extensive dialysis brings about an equilibrium where the bulk solution does not contain, or contains only a very small residual amount of, Mg ions.

FT-IR Spectroscopy Measurements. The samples for FT-IR spectroscopy studies were prepared as follows. PG dissolved in chloroform was dried under a current of nitrogen, then dispersed in D_2O with no salt to give a final concentration of 10 mg PG/mL. This was followed by sonication in a refrigerated capped tube for 13−15 min as described above (Determination of the Adsorbed Ligand Concentration). $MgCl_2$ was then added to the vesicles preparations to make the final appropriate salt concentration. A drop (10−20 μL) of each of the samples was layered on 25 mm diameter BaF_2 plates. The infrared measurements were performed in a BOMEM FT-IR spectrometer, Model DA 3.2, equipped with a mercury−cadmium-tellurium detector (nitrogen-cooled) and a KBr beam splitter. In general, 100 interferograms were collected and coadded and the infrared spectra were obtained upon subtraction of the BaF_2 plate spectrum. Spectral resolution was 2−4 cm^{-1}.

The spectra were processed using the PE-GRAMS/2000 (3.01 B) version of GRAMS/386. Prior to data treatment the FT-IR spectra were corrected for their content in D_2O by a standard subtraction procedure.[15] Then a seven- or nine-point Spectra-Calc version (Galactic Industries Corporation, Salem, NH) of a smoothing function of Savitzky−Golay[16] was applied to the spectral data. Identification of the band maxima frequencies was first done on inspection of the smoothed FT-IR absorbance spectra followed by resolution enhancement analysis using second derivative spectra obtained from calculations with the Spectra-Calc program.

3. Results and Discussion

3.1. Mg(II) Adsorption to PGV. We note first that the Mg ion induces the aggregation of the PG vesicles at concentrations above a threshold (T_c) that is between 7 and 10 mM (cf. Figure 3 of ref 2). The adsorption data reported here, which were obtained at cation concentrations below T_c, were therefore corrected for the effective surface of the lipid vesicles, that is, the surface that is accessible to lipid−Mg(II) interactions (see discussions in Papahadjopoulos et al.[17]). The correction factor is about 1.5, i.e., the average outside/inside surface ratio of small, unilamellar vesicles.[13b,18] Above T_c no correction is necessary, since the aggregation process is followed by fusion, which involves lysis and the reorganization of the lipid bilayers,[17] thus making the great majority, if not all, of the PG molecules available for binding with the Mg ion.

A second correction concerns the ionic strength of the vesicles solutions. This is necessary, since only 35−45% of the initial concentration of the divalent cation is dissociated (see Skoog and West[19]) and therefore capable of complex formation with the polar head group of PG. The activity coefficient (γ) is obtained from the Debye−Hückel expression[19]

$$\log \gamma = (-0.5085Z^2\mu^{1/2})/(1 + 0.3281\alpha\mu^{1/2}) \qquad (1)$$

where Z is the charge of the ion, μ the ionic strength, and α the effective diameter of the hydrated ion in Å units. The ionic activity (A) is given by

$$A = \gamma C \qquad (2)$$

where C is the molar concentration of $MgCl_2$. The ionic activity A is then used in the calculation of the association constant, K, for the interaction of Mg(II) with PG vesicles, and the maximum number n of Mg(II) binding sites per phospholipid molecule. To this end, we applied the inverse law of mass action (see Scatchard[20])

$$1/\upsilon = 1/n + 1/(nKA) \qquad (3)$$

where υ is the number of Mg ions bound per lipid molecule at various $MgCl_2$ concentrations. The results of calculations indicate that n is 0.123 or approximately one Mg(II) bound per eight PG molecules (see Figure 1 and Table 1). This is a most

TABLE 1: Coordination and Adsorption Data of Mg(II) in a Crystal Lattice (A) and a Model Phosphatidylglycerol Bilayer Membrane (B)

parameters[a]	units	coordination data A			adsorption data B	ref
CN		4	6	8		10
cr	pm	71	86	103		10
U_0	kJ mol^{-1}	1519	1254	1047		this work[b]
n [=Mg(II)/PG]					0.123	this work
n_0 [=PG/Mg(II)]					8.1	this work
U_0/PG[c]	kJ mol^{-1}				129	this work

[a] Abbreviations: CN, coordination number; cr, crystal radius; n, maximum number of binding sites of the Mg ion per PG molecule; n_0, maximum number of PG molecules bound per Mg ion (see Figure 1); pm, picometer; U_0, lattice energy (see text, section 3.3). [b] The U_0's were calculated according to eq 7 (see text). [c] U_0/PG, lattice energy per PG molecule, i.e., U_0/PG = 1047/8.1 kJ mol^{-1} (data in A and B).

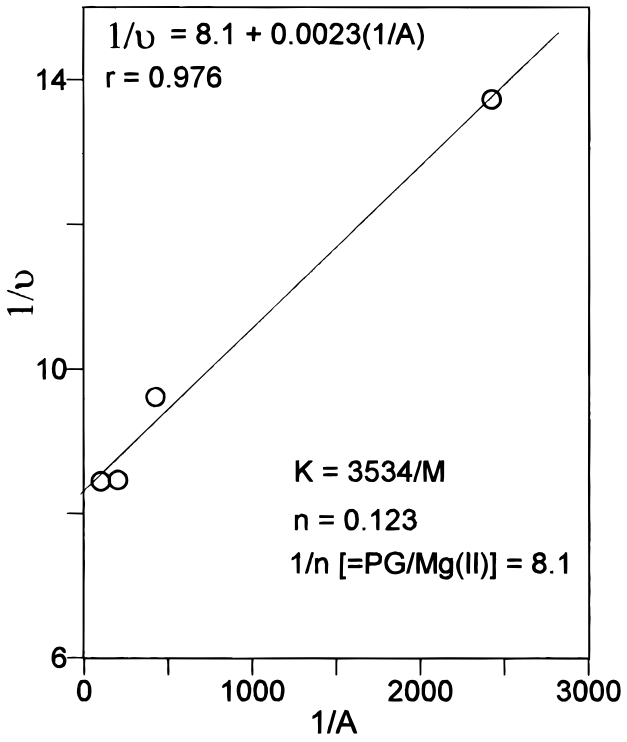

Figure 1. $1/\upsilon$ vs $1/A$ plot (see eq 3) for the fixation of Mg(II) on phosphatidylglycerol (PG) bilayer membranes. The measured final PG concentration is 340 ± 20 μM. The following are abbreviations defined: A, ionic activity; n, maximum number of Mg(II) binding sites per PG molecule; K, association constant; υ, number of Mg ions bound per PG molecule at various $MgCl_2$ concentrations.

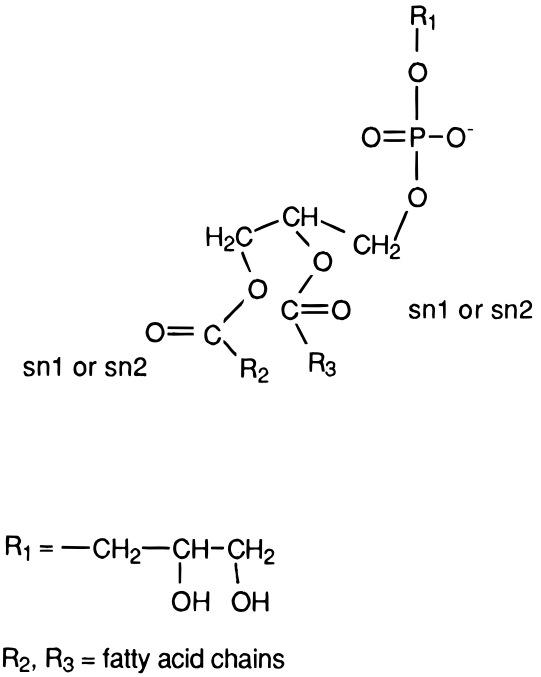

Figure 2. Chemical structure of phosphatidylglycerol: *sn*1, *sn*2 (see discussion in text).

interesting result, since it is directly related to the coordination number (CN) 8 of the Mg ion as determined from ionic lattice studies.[10]

3.2. FT-IR Studies. The vibrational modes in the 1750−1700 cm^{-1} region are assigned to the stretching modes of the carbonyl groups of the *sn*1 and *sn*2 fatty acid chains in PG[21] (cf. Figure 2). Figure 3 and Table 2 show that the ester C═O stretching vibration at about 1739 cm^{-1} observed in PG vesicles in the absence of salt is split into three bands with maxima at 1735, 1725, and 1702 cm^{-1} upon addition of 2 mM $MgCl_2$. No further frequency changes were observed at concentrations higher than 2 mM.

The best assignment of the high-frequency vibrations at 1735 and 1725 cm^{-1} is most likely two different states of the carbonyl group (see discussions in Lewis et al.[21]). Nevertheless, one should also take into account that the 1735 cm^{-1} band can be as well attributed to the *sn*1 carbonyl, i.e., the C═O probably more deeply inserted in the hydrocarbon region of PGV, and the 1725 cm^{-1} band to the *sn*2 C═O ,which in that frame would be closer to the polar head group of PG. The low-frequency band at 1702 cm^{-1} results most likely from dehydration of the ester C═O region upon salt addition.[22] It is worth noting in this respect that it is not yet possible to decide unequivocally whether the C═O group interacts with a hydrated or a dried form of Mg(II). We remark finally that the region between 1780 and 1680 cm^{-1} of the PG vesicles incubated in the presence of Mg(II) is characterized by a considerable variation of the infrared intensities in contrast with the relative invariance of the band maxima frequencies (cf. Figure 3). This is a reasonable indication that the ester carbonyl of phosphatidylglycerol is a site of interaction of Mg(II) in PGV inasmuch as the intensity of an infrared absorption band is proportional to the square of the change in the dipole moment,[23] that is, the C═O dipole in PGV.

The region between 1300 and 1000 cm^{-1} in the infrared spectra of phospholipids is dominated by the phosphate group vibrations,[24] that is, the asymmetrical stretching mode ($\nu_a PO_2^-$) between 1250 and 1205 cm^{-1} and the symmetrical mode ($\nu_s PO_2^-$) around 1110−1085 cm^{-1}. Under the conditions of our experiments, one observes the $\nu_a PO_2^-$ mode at 1216 cm^{-1}, the $\nu_s PO_2^-$ mode at 1093 cm^{-1}, and the stretching mode of the P−O ester bond, νC−O−P−O−C, at 1063 cm^{-1} (Figure 4). The important spectroscopic probes are (i) the frequency of the νC−O−P−O−C mode (and maybe also the $\nu_s PO_2^-$ mode), which reflects the conformation of the torsional angles in the P−O ester bonds,[25] and (ii) the bandwidth and frequency of the $\nu_a PO_2^-$ mode, which reflect, respectively, the mobility and

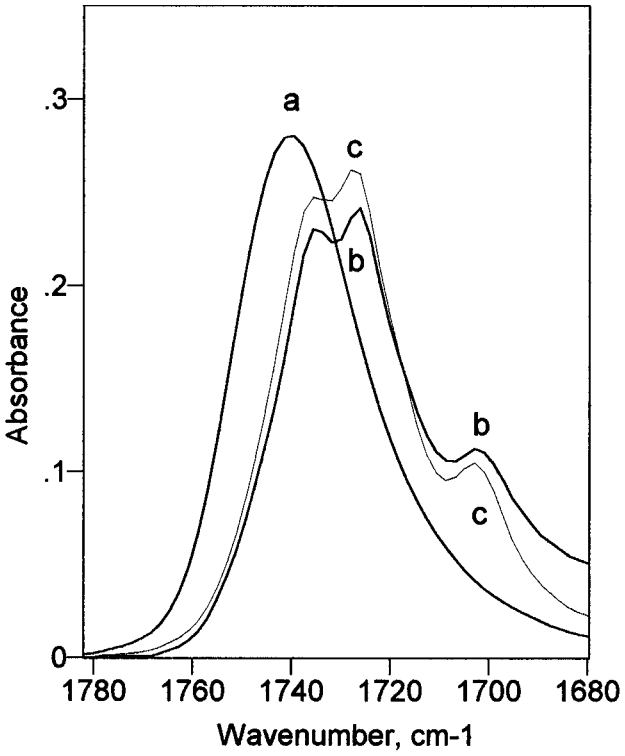

Figure 3. Ester C═O stretch region of FT-IR spectra of phosphatidylglycerol vesicles incubated without $MgCl_2$ (a) and with 2 (b) and 10 mM $MgCl_2$ (c). Spectra are normalized to the same integrated intensity.

TABLE 2: $MgCl_2$ Effect on the Band Maxima Positions between 1750 and 1000 cm^{-1} in the Infrared Spectra of Phosphatidylglycerol Vesicles

vibrational mode[a]	$MgCl_2$ concentration, mM				
	0	2	4	8	10
νC═O	1739[b]	1735	1735	1735	1735
		1725	1727	1727	1727
		1702	1702	1702	1702
$\nu_a PO_2^-$	1216	1259	1260	1261	1261
		1249	1252	1251	1252
$\nu_s PO_2^-$	1093	1108		1108	1108
νC−O−P−O−C	1063	1058		1060	1058

[a] $\nu_a PO_2^-$, asymmetric stretching mode of the PO_2^- group; $\nu_s PO_2^-$, symmetric stretching mode of the PO_2^- group; νC-O-P-O-C, stretching mode of the P−O ester bond; νCO, stretching mode of the ester C═O. [b] Wavenumber in cm^{-1}.

hydration degree of the phosphate group. In this context, the quite low $\nu_a PO_2^-$ frequency observed in our experiments, i.e., 1216 cm^{-1}, is an indication that the phospholipid head group in PGV might contain several bound H_2O molecules.[24d,e] Figure 4 displays the variation of the $\nu_a PO_2^-$ band maxima position with the $MgCl_2$ concentration present in the PGV preparations (see also Table 2). Table 2 shows that $MgCl_2$ induces a $\nu_a PO_2^-$ increase from 1216 to about 1261 (or 1252) cm^{-1} in PGV. These wavenumber shifts are peculiar because of two main effects. The first is a loss of water of hydration in the vicinity of the PG head group.[24d,25a] The second is a strong interaction between Mg(II) and the PO_2^- group in the phosphorylglyceryl moiety of PG.

It is essential to remark, in addition, that the variation of $\nu_s PO_2^-$ as a function of the $MgCl_2$ concentration as indicated in Table 2 points to the depletion of the phosphate group region of part of its hydration water upon $MgCl_2$ treatment. This is reflected in the displacement of $\nu_s PO_2^-$ from 1093 cm^{-1} in the absence of salt to an average value of 1108 cm^{-1} in the presence of 2−10 mM $MgCl_2$. However, these $\nu_s PO_2^-$ differences are much less marked than those observed with $\nu_a PO_2^-$ (see above) as is to be expected because $\nu_s PO_2^-$ is less sensitive than $\nu_a PO_2^-$ to variations in the chemical state of the phosphate group and its molecular environment.[24e]

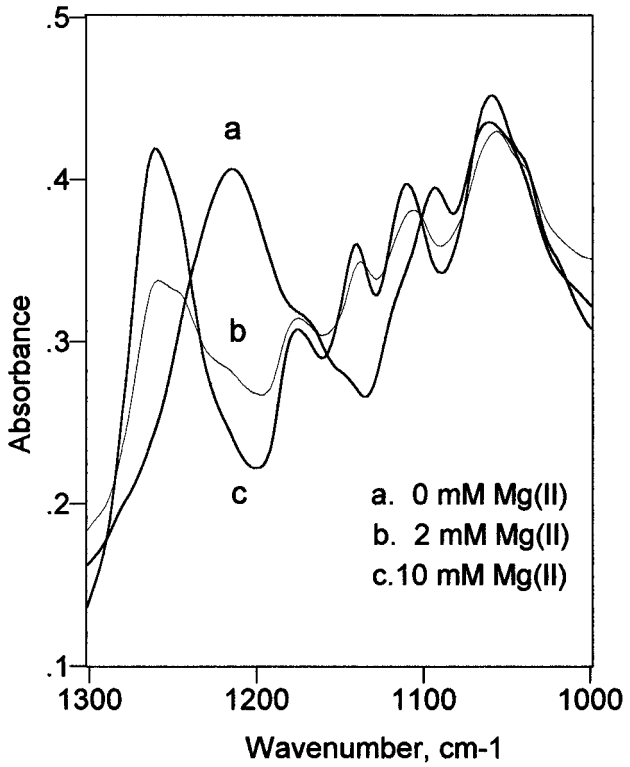

Figure 4. Phosphate stretch region of FT-IR spectra of phosphatidylglycerol vesicles incubated without $MgCl_2$ (a) and with 2 (b) and 10 mM $MgCl_2$ (c). Spectra are normalized to the same integrated intensity.

3.3. Modeling a Mg(II)−*n*PG Lattice in PGV. We showed above (section 3.1) that extensive dialysis of solutions of PG vesicles incubated with $MgCl_2$ brings about an equilibrium where the bulk solution does not contain any appreciable amount of free Mg ions, contrary to the systematic presence of Mg(II) in the PG bilayer membrane. It is thus plausible to assert that the dialysis procedure cannot deplete the phospholipid membranes of the Mg ions bound, or adsorbed, to the phosphorylglyceryl moiety of PG. In a study of ion−lipid interactions in bilayers constituted of digalactosyldiacylglycerol (DGDG), a nonionic lipid of the thylakoid membrane, it became clear[26] that any effect of this kind is attributable to the strong interactions that prevail in the low-polarity interface of the lipid bilayers, say, dielectric constant (ϵ) values of 25−to 32 (see, for example, refs 11 and 12). The calculations were made[26] by applying Born's expression for the total energy of charging an ion, $\Delta\mu$,[27] to the case of a change in free energy on transferring the ion from a medium of low dielectric constant, e.g., the water−DGDG interface ($\epsilon \approx 25-32$),[11,12] into one of high dielectric constant, e.g., the bulk aqueous solvent ($\epsilon \approx 78$). The results indicate[26] that $\Delta\mu$ is between −27 and −18 kJ mol^{-1}, meaning that the diffusion of the ion out of the water−lipid interface, i.e., H_2O−DGDG, into the aqueous phase is energetically favored but does not occur. A straightforward conclusion is that the energy resulting from the formation of an ion−lipid lattice is sufficient to retain the adsorbed ions bound to the lipid matrix (see discussion below). However, the molecular visualization of this structural framework is not easy. We attempt hereunder to elucidate this question further. For this purpose, we use, as a first approximation, a model ion lattice of the crystal type.[28]

We start with the concept that the stability of an ionic lattice can be determined from the Coulombic interactions among the ions, e.g., the ions in a Mg(II)−phosphorylglycerol lattice. Then we apply the Born expression of the potential energy (PE) for a pair of ions with charges Z_1 and Z_2 of appropriate sign[28b]

$$\mathrm{PE} = Z_1 Z_2 e^2/d + be^2/d^m \quad (4)$$

where e is the charge of the electron, d is the internuclear separation, m is a Born exponent (∼8−9 for the Mg ion[28b]), and b is a repulsion coefficient. Taking into account the forces of all neighboring ions in the lattice, the potential energy becomes

$$\mathrm{PE} = Ae^2Z^2/d + Be^2/d^m \quad (5)$$

where A is the Madelung constant[29] and B the repulsion coefficient. At the most stable equilibrium position of the ion, i.e., for $d = d_0$, PE is a minimum (PE_0). The expression of PE_0 is obtained by differentiating PE with respect to d, equating the result to zero, and making several substitutions (see details in ref 28b). PE_0 is then

$$\mathrm{PE}_0 = (Ae^2Z^2/d_0)(1/m - 1) \quad (6)$$

The lattice energy, U_0, is the potential energy when all molecules lie at their lattice sites. U_0 is an important factor in the stability of ionic solid substances. We will apply this concept to the head group interface of the PG bilayers (see, in this respect, ref 11).

U_0 is usually given as $U_0 = -\mathrm{PE}_0 N$. Hence,

$$U_0 = (NAe^2Z^2/d_0)(1 - 1/m) \quad (7)$$

where N is Avogadro's number. A simple calculation was performed using $d_0 = 2 \times \mathrm{cr}$, where cr is the Mg(II) crystal radius[30] given in Table 1 for CN = 4, 6, or 8. The values of m, Z, and A were 8, 1, and 1.75, respectively (see discussions in ref 28b), and e and N have the usual values. The results of the calculations are displayed in Table 1. It is seen that U_0 is 1519, 1254, and 1047 kJ mol^{-1} for CN 4, 6, and 8, respectively. U_0 is a minimum for CN 8, which is about identical with $n_0 =$ 8.1 (Table 1), therefore indicating that a Mg(II)−8PG lattice where Mg(II) coordinates with eight PG molecules is the most probable structural and geometrical arrangement of PG in the phosphatidylglycerol bilayer.

We remark finally that the lattice energy per PG mole, i.e., U_0/PG, is about 129 kJ mol^{-1} (cf. Table 1), which is much higher than the Born's energy of charging an ion, $\Delta\mu$, i.e., between −27 and −18 kJ mol^{-1} as was discussed above (see also ref 26). The calculations are therefore consistent with the experimental observation that extensive dialysis cannot extrude the bound Mg ions out of the phosphorylglyceryl moiety of PG (cf. section 3.1). On the other hand, the ion−lipid interactions described here bring about the minimization of the opposing forces, that is, the difference attractive forces minus repulsive forces, which prevail between the hydrocarbon core and the lipid head group and are responsible for the near equilibrium state of the bilayer membrane (see discussions in Tanford[31]). We conclude that the Mg(II)−8PG lattice concept developed here is a new molecular or fractal set, e.g., a Mandelbrot set,[32] that will be instrumental in modeling the membrane structures and geometries that minimize the opposing forces responsible for the lipid bilayer stability.[31]

4. Concluding Remarks

A major conclusion in this work is the finding that Mg(II) binds, or coordinates, with eight phosphatidylglycerol molecules. We showed that this is related to the coordination number (CN) 8 of the Mg ion in a crystal lattice. Calculation of the lattice energy for CN = 4, 6, and 8 indicates that the Mg ion adopts the lowest energy configuration, that is, a Mg(II)−8PG lattice for CN = 8. From the FT-IR study performed in this work we visualize the lattice as the result of interactions involving the Mg ions and the negative charge in PO_2^-, the oxygens in C−O−P−O−C and C−O−C (cf. Figures 3 and 4, and Table 2; see also discussions in refs 11 and 26), and the *sn*1 and *sn*2 C═O's (cf. Figure 2). However, the detailed structure of the Mg(II)−8PG lattice has yet to be determined experimentally, or at least worked out with molecular modeling and energy minimization methods (see, in this respect, ref 33). Nevertheless, its biological significance is obvious, since a CN of 8 ensures the greatest mobility of the PG molecules in the metal ion−lipid head group lattice described above.

Finally, a compelling corollary is whether the coordination properties of Mg(II) in the hydrophobic pocket of the D1 protein in the reaction center of PSII (see Kruse and Schmid's model[5]) are instrumental in the stabilization the PG molecules incorporated into the D1 protein on one hand and whether the membrane lattice effect is related to the enhancement by the Mg ion of the oxygen evolution in PSII (see refs 1 and 2) on the other hand. Evidence indicating that this could be so is given in a recent FT-IR work showing that the presence of Mg(II), or some kind of Mg ion pairs, in the lipid−protein interface of a PSII−PG complex favors the optimal function of photosystem II.[34] This will be discussed further in a forthcoming study of the effect of PG and Mg(II) on the PSII complex depleted of the 17 and 23 kDa extrinsic proteins (Fragata, Nénonéné, Méthot, unpublished results), that is, a molecular system close to the PSII complex of *Cyanobacterium* used by Kruse and Schmid.[5]

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