Detection of hexagonal phase forming propensity in phospholipid bilayers

Dear Sir:

In the August, 1992, issue of *Biophysical Journal,* Han and Gross (1992) presented an interesting study illustrating the sensitivity of the fluorescence anisotropy of certain labelled lipids to the lamellar to hexagonal phase transition temperature (T_h). The results illustrate a marked change in the temperature dependence of the fluorescence anisotropy close to T_h. Below T_h the fluorescence anisotropy decreases with temperature, while above T_h it increases. According to this paper, the temperature at which this change occurs agrees very well with the range of values for T_h reported in the literature using other methods. However, if one selects the most recent and most reliable values for the T_h of the synthetic diacylphosphatidyl-ethanolamines, which show a sharp phase transition, there is in general some discrepancy. For example, dielaidoylphosphatidylethanolamine has a T_h of 65.6°C, by DSC independent of heating scan rate and 63°C by a cooling scan at the slowest rate available marking the lower limit for T_h (Epand and Epand, 1988). This is still several degrees higher than the 58 ± 1°C found by fluorescence anisotropy. Similarly, 1-palmitoyl-2-oleoyl phosphatidylethanolamine has a T_h of 72.1°C or a lower limit of ~70.5° by cooling scans (Epand and Epand, 1988). Again, fluorescence anisotropy gives a lower value of 67 ± 1°. Only dioleoyl phosphatidyl-ethanolamine has a change in fluorescence anisotropy which agrees well with published values of T_h. Although we cannot provide a good explanation for why the fluorescence anisotropy for this lipid does not deviate from T_h, this lipid also differs in that its fluorescence anisotropy is significantly higher near T_h than it is for the other synthetic diacyl lipids. The discrepancy between the change in the temperature dependence of the fluorescence anisotropy and T_h is reminiscent of a recent report by Epand and Leon (1992), which demonstrated that the fluorescence properties of N^{ϵ}-dansyl-L-Lys and of Laurdan exhibit marked changes at temperatures several degrees below the T_h of dipalmitoleoyl phosphatidylethanolamine. These differences may have particular significance because it demonstrates that membranes with marked propensity for converting to the hexagonal phase, but while still in the bilayer phase, will have markedly altered surface properties. This may help to explain why in many cases the activity of membrane-bound enzymes and membrane fusion are accelerated by the presence of non-bilayer forming lipids in membranes which remain in the bilayer phase (Epand, 1991).

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REFERENCES

Epand, R. M. 1991. Biological consequences of alterations in the physical properties of membranes. In Cell and Model Membrane Interactions. S. Ohki, editor. Plenum Press, New York. 135–147.

Epand, R. M., and R. F. Epand. 1988. Kinetic effects in the differential scanning calorimetry cooling scans of phosphatidylethanolamines. *Chem. Phys. Lipids.* 49:101–104.

Epand, R. M., and B. T.-C., Leon. 1992. Hexagonal phase forming propensity detected in phospholipid bilayers with fluorescent probes. *Biochemistry.* 31:1550–1554.

Han, X., and R. W. Gross. 1992. Nonmonotonic alterations in the fluorescence anisotropy of polar head group labelled fluorophores during the lamellar to hexagonal phase transition of phospholipids. *Biophys. J.* 63:309–316.

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