

**INCREASING SURFACE CHARGE DENSITY INDUCES  
INTERDIGITATION IN VESICLES OF CATIONIC AMPHIPHILE AND  
PHOSPHATIDYLCHOLINE<sup>#</sup>**

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Binary vesicles of cationic lipid dihexadecyldimethylammoniumbromide (DHAB) and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC) were examined by differential scanning calorimetry, fluorescence spectroscopy, and Fourier transform infrared spectroscopy. DHAB/DMPC vesicles demonstrate a complex dependence of the main transition temperature ( $T_m$ ) on their mole proportion of DHAB, with a maximum of 42°C at  $X_{DHAB} = 0.4$ . Increase of  $T_m$  at  $X_{DHAB} < 0.4$  is explained by reorientation of P-N<sup>+</sup> dipoles of the phosphocholine headgroup resulting in tighter packing of the acyl chains, which increases the thermal energy required for *trans*→*gauche* isomerization. At  $X_{DHAB} > 0.4$  coulombic repulsion between the cationic DHAB headgroups expands the bilayer evident as a decrease in  $T_m$  until a plateau of approx. 28°C at  $0.7 \leq X_{DHAB} \leq 0.9$  is reached, followed by an increment of  $T_m$  to approx. 30°C at  $X_{DHAB} > 0.9$ . The quenching of DPH-PC fluorescence emission and decrease in the ratio of peak height intensities of symmetric and antisymmetric -CH<sub>2</sub>- stretching modes suggest interdigitated phase to form at  $X_{DHAB} > 0.6$ . Interdigitation allows the membrane to accommodate the augmented coulombic repulsion between DHAB headgroups due to increasing cationic surface charge density while simultaneously causing tighter packing of the acyl chains evident first as a plateau at  $0.7 \leq X_{DHAB} \leq 0.9$  and subsequently as an increase in  $T_m$  at  $X_{DHAB} > 0.9$ . Screening of the membrane charges by NaCl abolishes the quenching of DPH emission and decreases  $T_m$  thus revealing electrostatic repulsion as the driving force for interdigitation.

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