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Influence of polar head groups on the gel to liquid-crystal transition in vesicular and lipid bilayer systems

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Bilayer systems in aqueous solutions formed by the C₁₈-bilayer systems, dimethyldioctadecylammonium bromide (DOAB), sodium dioctadecylphosphate (DOP) and distearoyl phosphatidylcholine (PC) undergo well characterised gel to liquid-crystal transitions. Differential scanning microcalorimetric data yield melting temperatures, enthalpies of fusion and patch numbers for these systems which probe the effects of the polar head groups, since in each of these systems the chain lengths are similar. The patterns confirm unambiguously that the stability of vesicular systems reflects a balance between the stabilising effects of alkyl chain-alkyl chain cohesive interactions and the unfavourable charge-charge interactions between the polar head groups.

In aqueous solutions, amphipathic solutes having two long hydrophobic alkyl chains usually form interesting bilayer systems.¹ Differential scanning microcalorimetry (DSC) probes interactions between alkyl chains in the bilayers and we have examined the influence of alkyl chain length on the gel to liquid-crystal transitions for vesicular systems formed by sodium dialkylphosphates.² These transitions are characterised by a melting temperature T_m and a patch number n describing the number of monomers in each domain which undergo co-operative melting.² Within a given series of (sodium) dialkylphosphates, T_m increases with increase in alkyl chain length, confirming the general conclusion that hydrophobic alkyl chain-alkyl chain interactions are a source of bilayer stability. Here we report DSC data for three bilayer systems which have similar chain lengths but different polar head groups, (Scheme 1). This type of comparison highlights the role of hydrophobic cohesion and head-group interactions in important bilayer systems.

Experimental

Calorimetry

The DSC experiments were carried out using a MicroCal (USA) calorimeter as described previously.^{3,4} The differential

heat capacities were recorded for aqueous solutions containing DOP, DOAB or PC having the same concentration, $2 \times 10^{-3} \text{ mol dm}^{-3}$. The scans were recorded between 20 and 90 °C with a scan rate of 60 °C h⁻¹.

Materials

The DOP (sodium) was synthesised as previously reported;⁵ DOAB (Aldrich) and PC (Sigma) were used as received. The vesicular solutions for DOAB and DOP were prepared using the previously described 'hot-water' method.^{2,4} The PC system was prepared using sonication for 30 min at room temperature.

Results

The recorded scans for DOP, DOAB and PC systems were reversible over a series of heating-cooling-heating cycles (Fig. 1). Thus the phenomenon responsible for the extrema are reversible in the thermodynamic sense, in contrast to similar extrema recorded for aqueous enzyme solutions where the

Scheme 1

Fig. 1 Differential heat capacities for three solutions ($2 \times 10^{-3} \text{ mol dm}^{-3}$) as a function of temperature for (a) DOAB, (b) PC and (c) DOP; the plots have been displaced for clarity on the heat capacity (dC_p) axis

denaturation process is not normally reversible. The three key features are extrema at 44.7 (DOAB), 51.5 (PC) and 77.1 (DOP) °C, each linked with an intravesicular gel to liquid-crystal transition. The three derived parameters are melting temperature, T_m , patch number, n , and enthalpy of fusion, $\Delta_f H^\circ$. Analysis of the curves shown in Fig. 1 yields the following information; (i) DOAB, $T_m = 44.8 \pm 0.1$ °C, $n = 210 \pm 10$ and $\Delta_f H^\circ = 37.2 \pm 0.3$ kJ (monomer mol)⁻¹, (ii) PC, $T_m = 51.5 \pm 0.1$ °C, $n = 59 \pm 3$ and $\Delta_f H^\circ = 49.2 \pm 1.1$ kJ (monomer mol)⁻¹ and (iii) DOP, $T_m = 77.1 \pm 0.1$ °C, $n = 63 \pm 0.1$ and $\Delta_f H^\circ = 41.9 \pm 0.1$ kJ (monomer mol)⁻¹.

Discussion

The DSC curves shown in Fig. 1 provide a clear indication of the complicated features which determine the gel to liquid-crystal transitions in these bilayer systems. If the packing of the alkyl chains is broadly similar, the change in the parameters calculated from the DSC curves would be expected to reflect interactions between the head groups. In terms of T_m , this would suggest that head group repulsion is greater for DOAB and weakest for DOP, although the larger patch number for DOAB indicates greater cooperativity within the chains during the melting process. The shift in T_m possibly reflects the opportunity for charge delocalisation in the dialkylphosphate, tending to reduce the impact of charge-charge repulsion. Nevertheless, the derived enthalpies associated with the three transitions are similar. The role of the head groups

and associated head-group repulsion can be placed in context of the stabilising effects of alkyl chain-alkyl chain interactions. Thus, the shift of 32 °C on going from DOAB to DOP can be compared with the shift of 42 °C on going from C₁₈/C₁₈ ($T_m = 77.1$ °C) to C₁₂/C₁₂ ($T_m = 34.8$ °C) for sodium dialkylphosphates.² The balance between the crucial hydrophobic interactions between the alkyl chains and the unfavourable interactions of the head groups that are, to varying degrees, offset by counter ion binding has been clearly demonstrated in this study.

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