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DSC-STUDY ON THE INFLUENCE OF CHEMICAL ENVIRONMENT ON THE STRUCTURE OF LYOTROPIC LIQUID CRYSTALS

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INTRODUCTION

Differential scanning calorimetry (DSC) has proven an excellent technique in studies of the thermal behaviour of lipid-water systems which can be regarded as simple but useful models of the lipid matrix of cell membranes (for reviews, see 1,2). The model systems as the natural membranes show the characteristics of lyotropic liquid crystals (3). A prominent representative of lipids, dipalmitoyl-phosphatidylcholine (DPPC), which is among others the main phospholipid in lung alveolar surfactant (4) for instance shows three distinct phase transitions in the temperature range of 10-50°C. The most studied gel-liquid crystalline transition takes place at 41.5°C. Structural alteration in the lipid matrix which reflect in the thermograms connect to changes in the iontransport of the membrane (5) and to changes in the function of membrane proteins (6). In this work we investigated the thermal behaviour of several lipid-water systems modified by changing the pH-value and the ionic composition of the environment or by chemical agents like nonionic tenzides and some new crown ethers.

MATERIALS AND METHODS

DSC-measurements were made with a DuPont 910 DSC cell with a heating rate of 5°C/min and in the sensitivity range of 0.1-0.2 mW/cm. The samples were made by suspending the lipid powder in the appropriate amount of bidistilled water or salt-solution or solution of other chemical agents. The samples were kept above the phase transition temperature of the lipid component for 30 min before loading them into the Al-crucible for the calorimetric runs.

The intercept of the base line with the slope of the peak in the heating curve is given as the transition temperature. The area for the enthalpy calculation was determined by planimetry.

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RESULTS AND DISCUSSION

In the case of lipid molecules with one or more dissociable protons the variation of the pH-value of the system affects the interaction between the head groups of the lipid molecules. Phosphatidic acid (PA) which has two dissociable protons has been investigated. On increasing the pH-value from 3.5 to 9 the degree of dissociation increases from 0.5 to 1.5. Due to the increasing electrostatic repulsion between the head groups the gel-liquid crystalline transition temperature decreases as the cooperative unit size of the transition does too. Further increase in the pH causes an abrupt drop in the transition temperature which can be explained with the suggestion (7) that the hydrocarbon chains of lipid molecules tilt from the normal of the bilayer.

Also the polar head-group region of the lipid bilayer can be affected with monovalent ions. Table I shows that the chloride salts of alkalines increase the phase transition temperature (T_m) of dipalmitoyl phosphatidylethanolamine (DPPE) and to less extent that of DPPC. Other (nitrate and perchlorate) salts seem to be less effective.

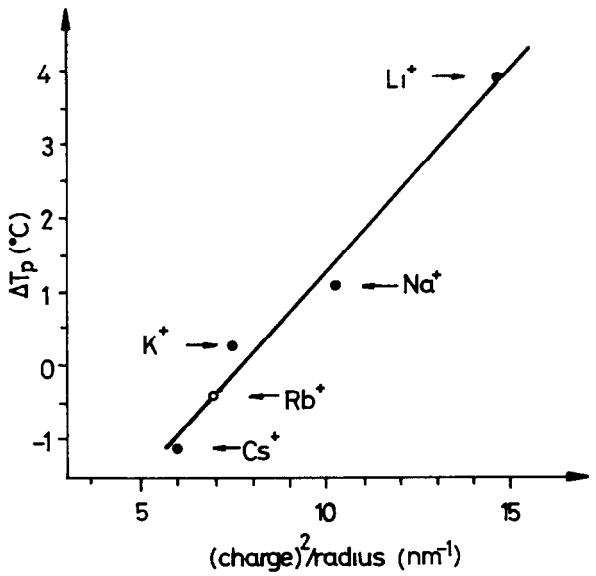
Table I

	DPPC	DPPE
water	41.5	63.5
3 M LiCl	43.1	67.1
3 M $LiNO_3$	41.3	65.5
3 M NaCl	43.0	68.0
3 M $NaNO_3$	41.1	66.0
3 M $NaClO_4$	41.4	-
3 M KCl	42.9	68.3
3 M KNO_3	41.4	65.3
3 M RbCl	42.9	69.6
3 M $RbNO_3$	40.9	66.0

We assume that the Cl^- ions promote the formation of H-bonds between the head groups stabilizing the gel phase. The effect increases with increasing salt-concentration (8).

An other phase transition (smectic G → rippled structure) the so called "pretransition" of the DPPC is sensitive to the different alkali cations. The characteristic temperature of this transition (T_p) increases in the presence of alkali cations and the increase (ΔT_p) correlates well with the $(charge)^2$/radius-

-values of the cations (Fig.).



Chemical agents like nonionic tensides and some new crown ethers perturbate the lipid bilayers more strongly. The homolog series of polyoxy-ethylene compounds containing 4-30 ethylene--oxide groups per molecules (n_e) have been investigated (9). The tensides decrease the characteristic temperature of the gel-fluid phase transition of DPPC-water system and also decrease the enthalpy of the transition. The results show that the tenside molecules penetrate among the hydrocarbon chains of lipid molecules. This interaction depends on the ratio of hydrophobic and hydrophylic parts within the tenside molecule i.e. on n_e. The modifying molecules act as structural defects loosening the lipid packing density. As a consequence they increase the permeability of lipid vesicles predicting possible changes in the function of natural membranes under the influence of tensides. As an example the strict correlation between the permeability increasing effect and the structure disordering effect of nonyl--phenyl-ethylene-oxide molecules is demonstrated in Table II.

	T_m (°C)	perm.constant x 10^{-12} m/s
control	41.6	5.2±0.04
n_e = 4	38.9	5.3±0.04
n_e = 6	37.5	9.0±0.08
n_e = 9	38.9	12.0±0.09
n_e = 13	40.0	8.2±0.07
n_e = 23	40.7	6.0±0.05

Similar correlation has been obtained for some new crown ethers which show great ion selectivity (10).

CONCLUSION

Our and other's experimental results show that DSC is a powerful technique for the tudy of model membranes. Recent development of high-sensitivity instruments help this technique in becoming a powerful tool in the study of natural membranes and other biological systems too.

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