Towards an Equation of State for Cell Membranes Composed of Lipid like Molecules (DMPC*)

J. U. Keller, Institute of Fluid- and Thermodynamics,
University of Siegen, 57068 Siegen, Germany

R. Winter, Institute of Physical Chemistry I,
University of Dortmund, 44227 Dortmund, Germany

*1,2-Dimyristoyl-sn-glycero-3-phosphatidylcholine

Abstract

Biological membranes in a first approximation may be considered as double-layers of lipid molecules as for example phosphatidylcholine or triphospatidylcholine. These molecules have (electrically) polar "heads" and non-polar aliphatic "tails" often consisting of ethyl groups (-CH_2-). A simple model for a biological membrane is a double layer of lipid molecules whereabout the "heads" form the external surfaces of the membrane and the "tails" are oriented to the interior of the membrane. The volume of such a membrane in aqueous solution depends - at constant PH - value on the pressure (p) and the temperature (T) of the solution.

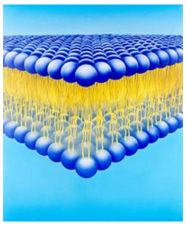
For a special DMPC*-membrane the specific volume has been measured at various pressures and different temperatures at the Institute of Physical Chemistry I of the University of Dortmund. Data show a phase transition whereby the "tails" in the interior of the membrane change their arrangement and motion from a chaotic, quasi-fluid state to a frozen, gel-like state with nearly parallel arrangement or self-adsorption of the CH_2-elements on their neighbouring groups. As the transport properties and the storage capacity of the membrane for water in both states differ considerably, knowledge of the phase transition data (p, v, T) is of importance for biotechnical and other applications. For the DMPC* membrane several sets of (p, v, T)-data have been measured at the University of Dortmund, namely isothermal (p, v) - data at 30°C, and isobaric (T, v) - data at p = 1 atm and the phase transition curve fluid – gel (p = p (T)). From these data a thermal equation of state has been developed at the Institute of Fluid- and Thermodynamics of the University of Siegen. Basic for this equation is the concept of (reversible) self adsorption of the lipids' tails on each other during the fluid-gel phase transition. This equation allows in principle to calculate the (specific) volume of the membrane at arbitrary temperatures (T) and pressures (p) and thus to get information on the fluid- or gel-state of the membrane.

In the presentation the equation of state will be given explicitly and its properties will be discussed to a certain extend.

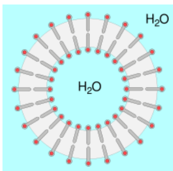
* 1,2-Dimyristoyl-s,n-glycero-3-phosphatidylcholin

Cell Membranes: Thermal Equation of State

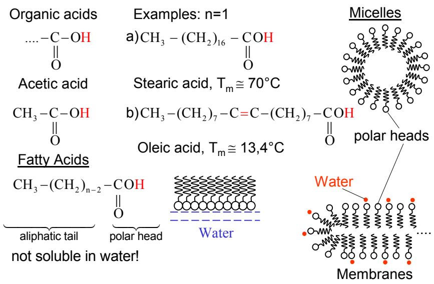
Double layer of lipid molecules
Polar „heads" – Non-polar „tails"



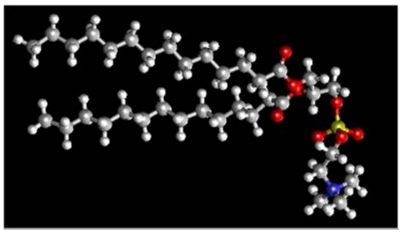
Lipid bilayer forming a micelle



Lipids, Fatty Acids: Elements of Biological Membranes



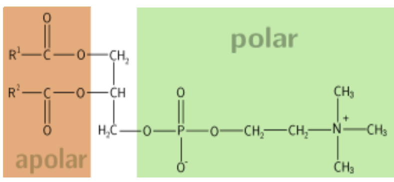
1,2- Dimyristoyl-sn-glycero-3-phosphatidylcholine



Ref.: R. Winter et al., JNE 32(2007), p.41…

Phosphatidylcholine / Lecithine

Fatty acids



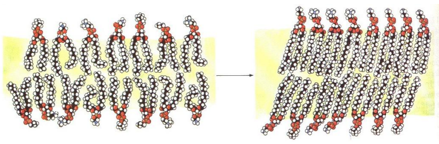
Glycerine CH2 – CH – CH2 / / / OH OH OH

Choline

DMPC: R1 = R2 = C14

Lipid Membranes, Phase Transition Fluid - Gel

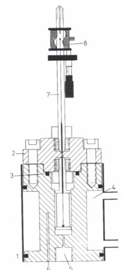
$T > T_t$ (p, ...) $T < T_t$ (p, ...)



Fluid-Phase Gel-Phase

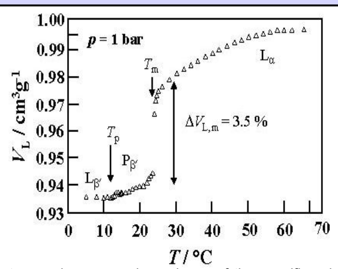
Lipid bylayer formed by phosphatidylcholine molecules (Voet&Voet, p. 288)

DMPC Solutions, pvT-Measurements
Volumetric Cell T = (0 – 100)°C, p < 250 MPa

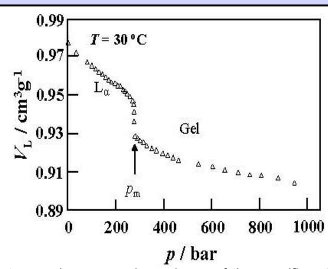


1 Pressure cell
2 Top flange
3 Viton O-ring
4 Thermostate
5 High pressure nut
6 Thermocouple inlet
7 High pressure pipe
8 Inductive coil

Ref. Böttner M. et al., High Pressure Volumetric Measurements on Phospholipid Bilayers, Z. Physik.Chemie 184(1994), p.205



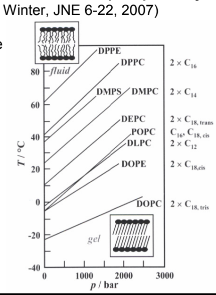
Temperature and pressure dependence of the specific volume of DMPC*) in water. (R. Winter, JNE 32(2007), p.41
*)1,2-dimyristoyl-s,n-glycero-3-phosphatidylcholine



Temperature and pressure dependence of the specific volume of DMPC*) in water. (R. Winter, JNE 32(2007), p.41
*)1,2-dimyristoyl-s,n-glycero-3-phosphatidylcholine

T,p- Phase Diagram of Various Phospholipid Bilayer Systems
(R. Winter, JNE 6-22, 2007)

Fluid Phase



Gel-Phase

DMPC Thermal Equation of State (EOS)

Aliphatic tails of DMPC-molecules may aggregate/adsorb on each other.

Degree of aggregation

$$\alpha(v) = \frac{v_0 - v}{v_0 - b_0} \qquad 0 < \alpha(v) < 1$$

Fluid state (v_0), Gel state (b_0)

Free volume

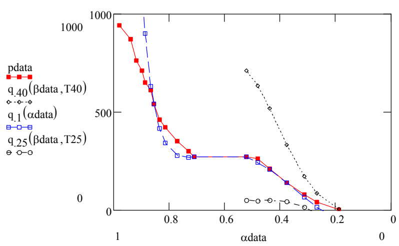
$$\beta(v) = \frac{v - b_0}{v_0 - b_0}$$

EOS: $$p(\alpha,T) = A(T)\cdot\alpha + B(T)\cdot\alpha^2 + D(T)\cdot\alpha^3 + C(T)\cdot\frac{\alpha^\gamma}{1-\alpha^\gamma} \qquad \gamma = 1$$

$$A(T) = A_0\cdot[1 + a\cdot(T - T_0)]$$
....
$$D(T) = D_0\cdot[1 + d\cdot(T - T_0)]$$

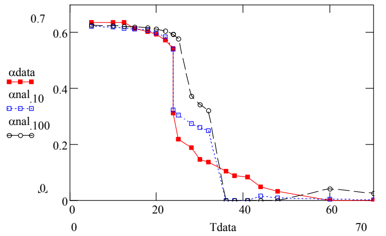
A = - 1873 bar	a = - 0.54
B = 7942	b = - 0.051
D = - 8997	d = - 0.429
C = 333.34	c = - 2.534

DMPC Thermal Equation of State (EOS)
Correlation of Isothermal Data



* R. Winter et al.,JNE 32(2007), p.41...

DMPC Thermal Equation of State (EOS)
Correlation of Isobaric Data



*R. Winter et al., JNE 32(2007), p.41...