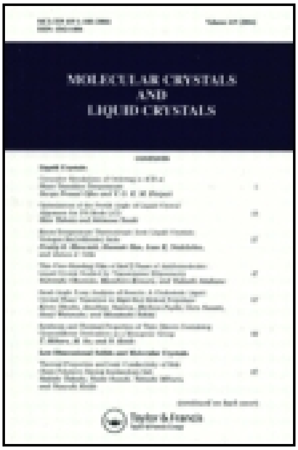

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Equilibrium Spreading Pressure of Steroids

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Equilibrium Spreading Pressure of Steroids

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Equilibrium spreading pressure (ESP) for the three kinds of steroids, i.e., (**I**) 5-cholesten-3β-ol, (**II**) 5α-cholestan-3β-ol, and (**III**) 5β-cholestan-3α-ol, was measured as a function of temperature and discussed thermodynamically in connection with their π-A relationships and the thermal results such as the melting point and the heat of fusion. It became clear that the direction of the OH moiety positioned at the 3rd-carbon atom of the steroid molecule gives a considerably large effect on the various thermodynamic properties in the solid states or in the monolayers on the water surface.

Keywords: equilibrium spreading pressure; π-A relationship; steroid

INTRODUCTION

Many lipids spread spontaneously when placed in a solid or liquid form at the water surface, thus giving monolayers in equilibrium with the excess bulk lipid phase. The corresponding monolayer surface pressure is generally known as the equilibrium spreading pressure (ESP). The ESP, which reflects the molecular structures and the state of the bulk such as a crystal or a liquid, is one of the important thermodynamic properties: Monolayer experiments carried out beyond the pressure of ESP are thought to be thermodynamically invalid.

In the present study, the ESP for the three kinds of steroids, i.e., (**I**) 5-cholesten-3β-ol (cholesterol), (**II**) 5α-cholestan-3β-ol (cholestanol) whose OH moiety is in the same direction to that of (**I**), and (**III**) 5β-cholestan-3α-ol (epicoprostanol) whose OH moiety is in opposite direction to that of (**I**), was measured as a function of temperature. The ESP values and the enthalpies for the spreading process of the steroid molecules from their crystals into their monolayers on the water surface were discussed in conjunction with their molecular structures.

Experimental Details

Samples of three kinds of steroids, **(I)** (purity > 99 %, Aldrich Co.), **(II)** (> 98 %), and **(III)** (> 95 %), were used without further purification. Chloroform (spectroscopic grade, Dojin Chemical Co.) was used as a spreading solvent. After the crystals of the sample were placed on a clean water surface, surface pressure, π, was measured with a platinum plate on an automatic surface tension apparatus (Kyowa Kaimen Kagaku Co., model CBVP-Z). Temperature dependence of π-A relationship was also measured using a temperature-programmable Langmuir trough.[1] The melting point and the heat of fusion for the steroid crystals were measured on the DSC apparatus (Rigaku Denki Co. Ltd., model 8230B).

Results and Discussion

Fig. 1 shows the time dependenc of π for the crystals of **(II)**. After an yield time, the π at a constant temperature increases rapidly and gradually reaches a constant value. This indicates that the steroid molecules would elute spontaneously from the crystals onto the water surface and finally produce a monolayer in equilibrium with the excess bulk phase. The constant π value was adopted as ESP. As shown in Table 1, the ESP for the each steroid increases with increasing temperature, T. By applying the two-dimensional Clausius-Clapayron Equation to the ESP-T relationship we obtained the enthalpy of the elution, ΔH_{ESP}, from the crystals into the monolayer at the surface pressure of

Fig.1 π for crystal of (II)

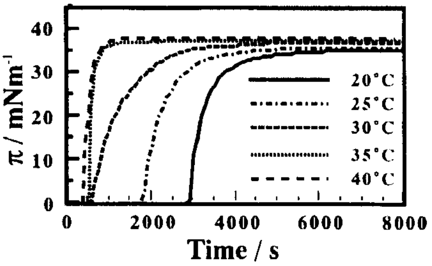


Table 1. ESP for Steroids

Temp. °C	(I) mNm^{-1}	(II) mNm^{-1}	(III) mNm^{-1}
20	32.1	35.2	13.5
25	33.0	35.8	13.8
30	34.7	37.0	14.3
35	35.7	37.4	14.7
40	36.6	37.9	15.1

the ESP. The ΔH_{ESP}, heats of fusion, ΔH_m, and the melting points of the steroid crystals are also listed in Table 2.

As can be seen in the Fig. 2, **(II)** whose OH group is in a same direction to that for **(I)** gives a same π-A curve as that for **(I)** at 25 °C, whereas the **(III)** whose OH group, in opposite direction to that for **(I)** gives an expanded one; the monolayer of **(III)** collapses at relatively low surface pressure.

Table 2. Thermodynamic Properties

	m.p. / °C	ΔH_m / kJ mol^{-1}	ΔH_{ESP} / kJ mol^{-1}	$-\Delta H_{comp}$ / kJ mol^{-1}	ΔH_{spread} / kJ mol^{-1}
(I)	149.5	26.5	17.8	1.24	19.0
(II)	140.7	22.6	10.3	0.51	10.8
(III)	112.8	15.8	6.8	0.36	7.16

Fig.2 π-A for Steroids

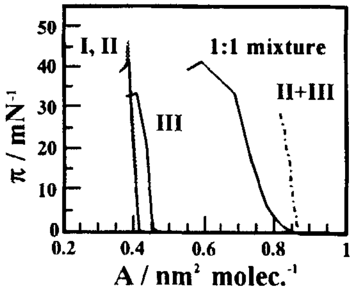
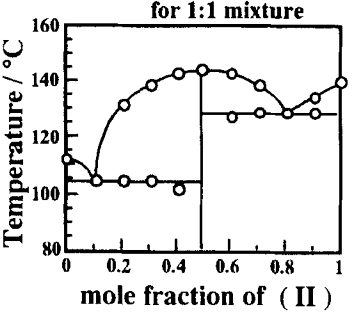


Fig. 3 Phase diagram for 1:1 mixture



From the temperature dependencies of the π-A relationships for the steroids, we evaluated the heats of monolayer compression: Integral from $\pi = 0$ to the pressure of ESP in the π-A curves at a constant temperature gives the work of compression, i. e., the Gibbs energy of compression, ΔG_{comp}. Application of the Gibbs-Helmholtz equation to the temperature dependence of the ΔG_{comp} gave the heat of monolayer compression, ΔH_{comp}. The sum of the ΔH_{ESP} and the (- ΔH_{comp}) means the heat of spreading, ΔH_{spread}, of the molecule from the crystal into the order-less monolayer at $\pi = 0$. The ΔH_{spread} values are also listed in the Table 2. **(I)** has larger values in ΔH_{ESP}, -ΔH_{comp}, and ΔH_{spread} than **(II)** or **(III)**. In other thermodynamic properties such as m.p. and ΔH_m,

(I) also has larger values than the (II) or (III). This would be attributable to the interaction due to the π-electrons between the double bonds of the cholesterol molecules in its crystalline and monolayer states.

The thermodynamic properties for (II) are relatively close to those for (I), while those for (III) are small and far apart from those for (I). This difference in the properties would come from the molecular structures of the steroids. In general, the steroids consist of four main rings; the four rings are termed **A**, which directly rinks an OH moiety, **B**, **C**, and **D**. The four rings of (I) or (II) are linked in all *trans*-form: Thus, the molecule of (I) or (II) looks just like a fat, straight rod. On the other hand, the **A** and **B** rings for (III) are linked in a *cis*-form; the **A**-ring part seems steeply bending against the molecular axis of the (III).[2]

As shown in Figure 2, the π-A relationship for the 1:1 mixture of compounds (II) and (III) seems to shrink: The molecular area for the 1:1 mixture at an arbitrary surface pressure is smaller than that expected as the sum (dashed line) of the areas for the (II) and (III). Thus, on the water surface, the molecules of (II) and (III) seem to interact with each other and produce the 1:1 compound especially at high surface pressure, because the π-A isotherm for the 1:1 mixture rises up at the same molecular area as the sum of those for the (II) and (III) and significantly shrinks at a higher surface pressure. The existence of the 1:1 compound was confirmed in solid state. As shown in the phase diagram in Fig. 3, the mixture of (II) and (III) gives a highest m.p. in 1:1 molar ratio: the steroids (II) and (III), whose OH moieties are in opposite directions with each other, make a strong 1:1 compound in the solid state. On the other hand, the straight rod-like (I) and (II), whose OH moieties are in the same direction with each other, do not form any compound; they make only a eutectic mixture in the crystalline form. Thus, the direction of the OH group positioned at the 3rd-carbon atom of steroid molecule apparently gives a large effect on the many thermodynamic properties in the solid state or even on the water surface.

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