

Short Communications

Further Investigations of Multimolecular Layers on Aqueous Surfaces

HENRIK BRUUN

Institute of Physical Chemistry, Abo Akademi, Abo, Finland

Surface balance studies¹ of the multimolecular layers of isodextropimaric acid have shown that when the collapsed monolayer is compressed from a dimolecular to a trimolecular layer, a transition from the liquid to the solid state takes place. A further compression leads to a rapid increase in the surface pressure, after which the trilayer appears to collapse.

Also multimolecular layers of other substances undergo on compression changes similar in many respects to those described for isodextropimaric acid. Fig. 1 gives the surface pressure-area curves recorded with the surface balance for tetrahydroabietic (I), dihydroabietic (II) and isodextropimaric (III) acids. The curves for tetrahydroabietic and dihydroabietic acids apply to layers supported on an alkaline substrate (pH 9.1), the curve for isodextropimaric acid on diluted hydrochloric acid (pH 3.0). It is seen that the curves for tetrahydro- and dihydroabietic acids resemble that obtained for isodextropimaric acid in that they show a rapid increase of the surface pressure in the compression region *c-d* and their multilayers appear to collapse at *d*. As in the case of isodextropimaric acid the tetrahydroabietic acid layer is solid in appearance just before

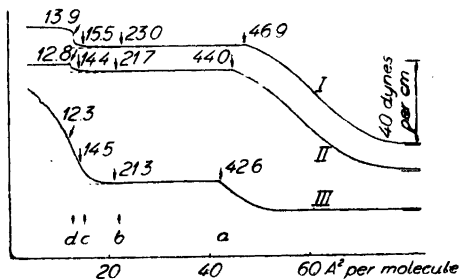


Fig. 1. Surface pressure-area curves of tetrahydroabietic (I), dihydroabietic (II), and isodextropimaric (III) acids. At point *a*: total collapse of the monolayer occurs, at *b*: the dilayer is completed, at *c*: the trilayer is completed, at *d*: the trilayer appears to collapse. Curves I and II have been taken on water containing 5 moles sodium chloride, $\frac{1}{100}$ moles sec. sodium phosphate per litre and sodium hydroxide to give pH 9.1; curve III has been recorded on dilute hydrochloric acid (pH 3.0). Temperature 20° C.

this collapse point. The first increase of the surface pressure appears to occur at *b*. Calculations¹ of the areas per molecule revealed that the isodextropimaric acid multilayers are dimolecular at point *b* and trimolecular at point *c*. The same appears to be the case with tetrahydro- and dihydroabietic acids as is evident from Fig. 1.

It seems that the observed phenomena cannot be explained by assuming that they are solely due to an increase in the thickness of the layers; the phenomena must be connected with marked changes in the inner structures of the layers. The relatively strong increase in pressure observed in the region *c-d*, which is specially marked in the case of isodextropimaric

acid, indicates a very stable arrangement of the molecules in the trilayer. The molecular arrangement shown in Fig. 2, B, which is similar in principle to those proposed for many built-up multilayers and micelles of association colloids, may explain the observed stability. This particular arrangement of the molecules in the trilayer is indicated by the fact that when multilayers of isodextropimaric acid containing different *n*-fatty acids are studied (mixtures containing 5, 10, and 20 mol per cent of the even *n*-fatty acids $C_{14}-C_{24}$ have been investigated²) the multilayer containing *n*-eicosanic acid ($C_{20}H_{40}O_2$) gives the most stable trimolecular layer, *i.e.* one that shows the highest surface pressure at point *d*. The length of the paraffin chain of the eicosanic acid molecule corresponds closely to the length of the hydrophobic parts of two isodextropimaric acid molecules, when built in the trilayer as shown in Fig. 2, B. When ionized molecules form the trilayer, as in the case of tetrahydroabiatic and dihydroabiatic acid on a substrate with a pH over 9, it is to be expected that water molecules and gegenions are incorporated between the hydrophilic groups of the trilayer. The presence of water molecules may explain the more liquid character of the multilayers on the alkaline substrate and also the fact that at higher temperatures (above 35°C) the trilayer arrangement is more stable on an acid substrate than on an alkaline one.

Fig. 2, A shows a possible arrangement of the molecules in the dilayer (at *b*), which takes into account the constancy of the surface pressure from *a* to *b*. The trilayer is formed from the dilayer by a gradual process on compression, which is indicated by the continuous increase in pressure from *b* to *c*.

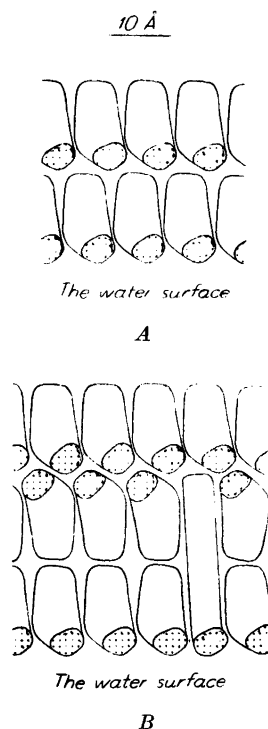


Fig. 2. Assumed molecular arrangement of the dilayer (A) and trilayer (B) of isodextropimaric acid. The carboxylic groups in the molecules are shaded. At the right, an eicosanic acid molecule is shown built in the trilayer.

It is possible that the study of the multilayers with the surface balance technique may throw light on problems in the field of the association colloids.

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1. Bruun, H. *Acta Chem. Scand.* **6** (1952).
2. Bruun, H. *To be published.*

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