# FINSKA KEMISTSAMFUNDETS MEDDELANDEN

# SUOMEN KEMISTISEURAN TIEDONANTOJA

REDAKTÖR — TOIMITTAJA

Tor-Magnus Enari


INNEHÅLL — SISÄLTÖ




N:o 1 • ÅRGÅNG 72 VUOSIK. • 1963

FINSKA KEMISTSAMFUNDETS MEDDELANDEN

**Annonspris**
på annonssidor 80:—
på sidor mot text 80:—
på bakpärmen 100:—

**Prenumerationspris**
i Finland 10:—
till utlandet 12:—

**Annonser och prenumerationsärenden**
Fil. mag. Karin Sandelin
Universitetets Virologiska institution
Fabiansgatan 24
Telefon 63 48 03

SUOMEN KEMISTISEURAN TIEDONANTOJA

**Ilmoitushinnat**
ilmoitussivuilla 80:—
tekstin vastaisella sivulla 80:—
takakannessa 100:—

**Tilaushinta**
Suomessa 10:—
Ulkomailla 12:—

**Ilmoitus- ja tilausasiat**
Fil. maist. Karin Sandelin
Yliopiston Virusopin laitos
Fabianinkatu 24
Puhelin 63 48 03

FINSKA KEMISTSAMFUNDETS MEDDELANDEN

SUOMEN KEMISTISEURAN TIEDONANTOJA

72 årg. 1963 N:o 1 72 vuosik.

Utgiven av — Julkaisija
Finska Kemistsamfundet — Suomen Kemistiseura
Postbox 476 Postilokero
Helsingfors — Helsinki

Styrelse — Hallitus
JARL GRIPENBERG — TOR-MAGNUS ENARI — TERJE ENKVIST
OLOF FORSANDER — CHARLEY GUSTAFSSON — JARL JOHAN LINDBERG
ALBERT SUNDGRÉN — JACOBUS SUNDMAN

Sekreterare — Sihteeri
NILS-ERIK SARIS, Näshöjdsvägen 10 B Niemenmäentie tel. 413411, 484999 puh.

Kassör — Rahastonhoitaja
KARIN SANDELIN, Universitetets Virologiska institution — Yliopiston Virusopin laitos
Fabiansg. 24 Fabianink. tel 34 803 puh

Arkivarie — Arkistonhoitaja
ANNA GRÖNVIK, S. Hesperiag. 4 E. Hesperiank. tel 44 01 01, 44 73 99 puh

Redaktör — Toimittaja
TOR-MAGNUS ENARI, Färdemannastigen 2 Matkamiehenpolku tel 55 022, 47 35 37 puh

# The First Scandinavian Symposium on Surface Activity

*Per Ekwall*

It is with the greatest pleasure that I bid you all welcome to this symposium on surface activity which it is my honour to declare opened.

## *The Aim and Organisation of the Symposium*

When the organisation committee of the Eleventh Scandinavian Chemist Congress (Elfte Nordiska Kemistmötet), at the suggestion of the Scandinavian Council of Chemistry, enquired in November last year whether I would be willing to organise a symposium in surface chemistry I at first was fairly hesitant to undertake this responsibility. It was not a question of a lack of interest on the part of my co-workers and me, but it was the fact that research work in the field of surface activity has

been carried out in only a few centres in Denmark, Norway, Sweden and Finland and it did not seem appropriate to arrange a symposium on subjects of interest to only a relatively small group of participants. I was therefore doubtful whether there was enough interest in problems of surface activity that it would justify the venture. The response to the first circular letter proposing such a symposium was, however, gratifying and showed that active cooperation could be expected, not the least in the area of applied surface chemistry.

From the very beginning it was, however, obvious that neither time nor resources would suffice to cover the whole field that is implied by the concept of a symposium in surface activity. Interfacial phenomena represent so extensive an area and are encountered in varying forms in so many branches of science and industry that it was possible to consider only certain limited topics as items for a programme. As this symposium was to be the first of its kind to be held in the four Scandinavian countries and as it is a fact that academic education in this field has been very limited, it seemed appropriate to organise the symposium so that it would provide a possibility to present general surveys of the present state of our knowledge in some central fields. In this way it was hoped that the programme would then arouse the interest of wider circles in this field of chemistry. Hence the items to be discussed were limited already at the outset. Extensive and important topics such as surface catalysis, chromatography and interfacial phenomena in biology had to be excluded. The final plan of the general part of the programme was determined by the persons available to function as lecturers. In addition to the reviews we intended to include shorter communications on specialised subjects. The number of the latter which participants proposed to present has exceeded by far our anticipations. In spite of the fact that the programme thus became crammed, it seemed desirable to include all the communications as evidence of the active interest displayed in the subject of the symposium. As the programme now stands, it should give a fairly good picture of the interest in surface activity and the work being done in various fields and on various complex problems in this discipline in our countries. Surface-active substances occupy a central position in this programme, but it is with satisfaction that one notes that many lectures will deal with phenomena that do not directly concern these substances. We have therefore, if with some misgivings, retained the original, although too comprehensive, name of a symposium in surface activity for our meeting.

At first it was our intention to hold the symposium in one of the auditoria of the Åbo Akademi. The large number of participants who preliminarily expressed their intention to attend the



symposium forced us, however, to seek a larger meeting place. The choice of this location, the grand hall of the old Academy building, arose from the desire to commemorate our eighteenth century chemist Johan Gadolin who may be considered the first chemist in Finland to study surface phenomena. After Scheele discovered the ability of charcoal to adsorb gases and Lowitz, an apothecary in St. Petersburg, soon after found that charcoal adsorbs compounds also from their solutions, Gadolin used birch charcoal to purify spirits, an application of surface chemistry that was later widely practised and is still practised in Finnish communities, or, perhaps more correctly, in backward rural districts in Finland. In the first years Gadolin worked in the chemistry laboratory which his predecessor Pehr Gadd equipped in a small house alongside the wall encircling the cathedral on a location just outside the entrence to this hall. When this building we are now in was erected for the Academy, Gadolin established a laboratory here. We may hence say that we are on historical ground from the point of view of surface chemistry.

*General Aspects of the Properties of Surface-Active Substances*

In order to save time it seems appropriate already in this opening address to say a few words about the general characteristics of surface-active substances. These compounds are amphiphilic, which means that they are both hydrophilic and lipophilic. Their molecules exhibit an affinity for and are to some extent soluble in polar as well as nonpolar solvents. These contrasting properties are, it is true, embodied in the same molecule, although they are possessed by distinct parts of the latter. The molecule contains a hydrocarbon part that is lipophilic by nature and another part consisting of one or more ionising or polar groups which are hydrophilic by nature. This dual structure is the reason for the special properties which here interest us.

The hydrocarbon part may vary in structure and the hydrophilic part likewise. Various combinations of hydrophilic and lipophilic groups are possible; the connecting link between them may also vary. A great diversity exists in these respects.

When these amphiphilic compounds dissolve in an aqueous medium, the following takes place. The polar water molecules which are bound by hydrogen bonds as loosely coherent, large aggregates are forced apart by the large hydrocarbon part of the surface-active molecule. This is associated with an increase in the free energy of the system which is counteracted by such an arrangement that the least possible number of water molecules are separated by the hydrocarbon part under the prevailing conditions at the same time as the hydrophilic groups to the greatest possible extent remain in contact with the water mole-

cules. This is attained in three different ways. *One* way is that some of the organic ions or molecules are so to say quenched out of the solution and accumulate at phase boundaries of the latter, where they arrange themselves with their hydrocarbon parts adjoining and more or less closely packed, often projecting out from the solution, and with their hydrophilic groups embedded in the water. *Another* way is that the molecules or ions associate within the solution to large aggregates, micelles, in which the molecules are more or less oriented side by side with the hydrocarbon parts pointing towards the centre of the micelle and the hydrophilic parts projecting outwards into the water. The *third* possibility is that mesomorphous phases are formed in which the molecules or ions are similarly oriented as in the micelles, but form much larger aggregates, which in turn are ordered with water between as a secondary structure. These three phenomena are to some extent coordinated and it is difficult to discuss isolated phase boundary phenomena without at the same time taking account of the phenomena occurring within the phases. Surface chemistry encompasses all these phenomena.

The name surface-active compound takes cognizance of the tendency of these compounds to concentrate at phase boundaries and in this way lower the free energy at these boundaries. The name association colloid points to the tendency of the compounds to associate to micelles. Molecular structure, the concentration of the substance and the properties of the environment are factors that determine which of the above-mentioned phenomena comes to the foreground. Of particular importance is the balance within the molecule itself. This hydrophilic-lipophile balance is determined in the first place by the molecular structure. A shift in the balance may, however, in some cases be effected by a change in the environment, for example, by a change in the hydrogen-ion concentration and by a change in the concentrations of other ions or molecules in the solution. A substance that may under certain conditions behave like a typical association colloid, may under other conditions behave like a predominantly lipophilic compound with weak hydrophilic properties which concentrates at phase boundaries but does not form micelles. On the other hand, such a substance may form micelles in a lipophilic envirronment although it may not form them in aqueous solution.

### *The Programme*

As our programme shows, the morning session is devoted to the three fundamental phenomena, matter at phase boundaries, in micelles and in mesomorphous phases. After a short review of the conditions in phase boundaries in general (Bruun), the conditions at phase boundaries in cases where the lipophilic



character of the molecules predominates to such an extent that they do not dissolve in water will be discussed (Lundquist). The next lectures will relate to phase boundary phenomena where the solubility in water must be taken into account (Koefoed, Harva, Bohn) and finally the conditions within various phases will be considered (Mandell, Ekwall, Danielsson, Fontell).

The afternoon session will be concerned with problems of technical interest. Attention will first be paid to the surface-active compounds and to their preparation and analysis (Matell, Schönfeldt, Johansson). A number of important surface-chemical phenomena of technical interest will then be reviewed (Groth, Hellsten, Sjöblom, Olsson) and the final papers will deal with a number of industrial problems of specialised nature (Bohn, Ekwall, Gärtner, Back, Tikkanen).

FINSKA KEMISTS. MEDD. 72 N:o 1 (1963) SUOMEN KEMISTIS. TIED.

# Monolayer and Molecular Structure

*Henrik H. Bruun*

*Institute of Wood Chemistry, Åbo Akademi, Åbo, Finland*

## *The Ubiquity of Phase Boundaries*

If our sense of sight were a million times more acute than it is, it would be possible for us to distinguish as small particles as individual molecules. We could then establish with our own eyes that we live in a world of phase boundaries. These surround even the smallest cell in the plant and animal kingdom and they delimit the individual crystals in the ores and rocks of the inanimate world. The apparently homogeneous sea water and air comprise an incalculable number of inhomogeneities which present limiting boundaries against the surrounding phases. Iron, steel, paper and textiles, to take a number of industrial products, are further examples of matter consisting of heterogeneous particles separated by phase boundaries.

By carrying out measurements and calculations we can draw a picture of the magnitudes of the areas of phase boundaries in systems of these types. The results are often surprising. For example, the total area of water droplets in fog is no less than sixty thousand square centimetres per cubic centimetre of air *(Table 1)*, the combined area of the red blood corpuscles in one cubic centimetre of blood is 5 square centimetres, the fat droplets in one cubic centimetre of milk have an area of 240 $cm^2$, silica gel, which serves as a model for the soil that covers the surface of our earth, has a surface of the order of 3 million square centimetres per cubic centimetre and the surface of chemical pulp is approximately 4 million square centimetres per gram.



*Table 1.* The magnitudes of interfacial areas in several common forms of matter.

| System | Nature of interface | Basis of calculation | Calculated surface area |
|---|---|---|---|
| Fog | Gas/liquid | Waterdrop diameter 0.01 $\mu$; 1 % water in air | $6 \cdot 10^4$ $cm^2/cm^3$ of fog |
| Milk | Liquid/liquid | Fat globules diameter 10 $\mu$; fat content 4 % | 240 $cm^2/cm^3$ of milk |
| Blood | Liquid/solid | Diameter of red corpuscles 8 $\mu$; $5 \cdot 10^6/cm^3$ of blood | 5 $cm^2/cm^3$ of blood |
| Silica gel | Gas or liquid/ solid | Absorption data | $3 \cdot 10^6$ $cm^2/cm^3$ of gel |
| Chemical pulp | Gas or liquid/ solid | External and internal surfaces of fibre cells [1] | $4 \cdot 10^6$ $cm^2/g$ of pulp |

## *Properties of Phase Boundaries*

Phase boundaries are characterized by three fundamental relationships. First, every unit of area of a phase boundary bears a definite amount of free energy; for water this free surface energy is 73 ergs per square centimetre. In the case of fog (Table 1) the water particles have a free surface energy of about 4.4 million ergs or 0.11 calorie per cubic centimetre. For practical reasons it is often customary to speak of surface tension instead of the free surface energy. They are dimensionally equivalent quantities.

The second aspect of a phase boundary is that the transition from one phase to an adjoining one is very sharp; statistically the phase boundary is only one or two molecules thick. This is a consequence of the very short distance over which the intramolecular forces of attraction, which determine the existence of the phase boundary, act.

The third aspect of a phase boundary is that it usually exhibits a potential difference; one phase carries a charge different from that of the adjoining phase. In contrast to the free surface energy and the thickness of the phase boundary, the magnitude of this potential difference is greatly dependent upon the external conditions.

## *Monomolecular Layers*

It has long been known that certain substances spread out over a water surface, whereas others do not. It is generally true that the spreading occurs if the energy of adhesion ($W_A$) between water and the substance in question is greater than the work of cohesion ($W_K$) of the compound. The tendency of the compound

to spread over the surface increases with the difference between these two amounts of work. This difference ($W_A - W_K$), which is a measure of the decrease in free surface energy associated with spreading, is known as the spreading coefficient S. Values of the spreading coefficient can be obtained from tables.

If the condition $S > 0$ is fulfilled, spreading will take place and a layer one molecule thick, a monomolecular layer, of the substance will be formed at the phase boundary.

If we consider the spreading from the point of view of molecular structure, the main factor that determines the spreading tendency is the presence in the molecule of atoms or atom groups of polar or ionic character. Compounds with highly polar groups such as hydroxyl, amine, carboxyl, and carbonyl groups mostly have high S values.

When the polar group turns toward the water phase — or when the phase boundary lies between two immiscible liquids, toward the phase with the higher dielectric constant — the molecules in the monolayer assume similar positions relative to one another. A monolayer is hence a form of matter in which there prevails a certain order. The forces of adhesion and cohesion promote the development of the order, whereas kinetic forces tend to disrupt the order.

The methods that have been employed to study the properties of monolayers are, for instance, the measurement of surface areas, potentials and viscosities with a surface balance, and optical, electron diffraction, x-ray diffraction and radioisotope measurements. Of these the surface balance method has given the most information about the relationships within monolayers.

By means of such measurements it has been found that, although the monolayer has primarily only two dimensions (the third is the thickness of the monolayer), the substance forming the monolayer may exist in different states of aggregation or phases. We have a gaseous, a liquid, a solid and, in addition, an expanded state. The last-mentioned is exceptional in that in the three-dimensional system it would mean that one litre of liquid could occupy also a volume of several litres.

## *Monolayer Structures*

Of fundamental importance for the understanding of the properties of a monomolecular layer is a knowledge of the arrangement of the molecules in the monolayer, i.e. the monolayer structure. This structure depends in the first place upon the structure of the molecules forming the monolayer, but it also depends on the magnitude of the phase boundary area available to the monolayer, on temperature and on the nature of the adjoining phases. When this area is neither very large or small, the



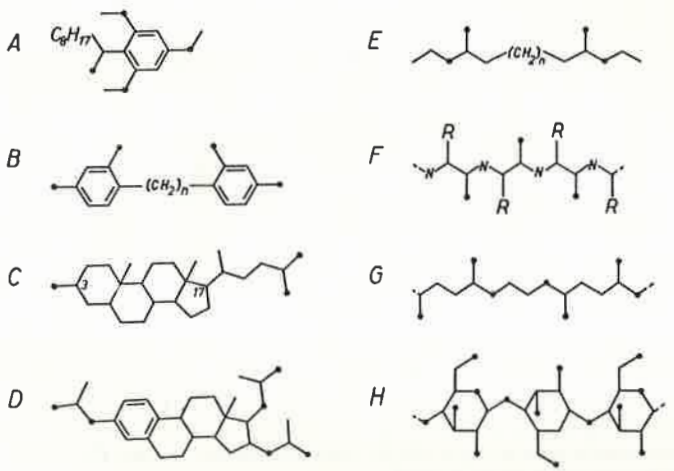



*Fig. 1, A—H.* Structures of molecules that assume a horizontal position on aqueous surfaces. Oxygen atoms and hydroxyl groups are indicated by black circles.

A Nonoyltrimethoxybenzene,
B 1,10-Diresorcinyldecane (n = 10),
C Bile acid of the litocholic acid type (litocholic acid),
D Oestriol triacetate,
E Long-chain dicarboxylic ester (n = 10, 11),
F A section of a protein molecule,
G A section of a poly(ethylene succinate) molecule,
H A section of a cellulose molecule.

temperature ambient and the phase boundary that between air and water, under which conditions most monolayer studies have been carried out, the following may be said about the relationship between molecular and monolayer structures.

*Monolayers of Horizontal Molecules.* Molecules that contain two or several polar groups distributed over them usually assume a horizontal position on an aqueous surface. Examples of such molecules are nonoyltrimethoxybenzene [2] (Fig. 1 A), 1,10-diresorcinyldecane [3] (B), bile acids of the litocholic acid type [4] (C), oestriol triacetate [5] (D), dicarboxylic acids [6] (E), and polymeric compounds with polar groups in the monomers such as proteins [7-11] (F), poly(ethylene succinates) [12] (G), cellulose (H) and cellulose derivatives [13-15].

*Monolayers of Upright Molecules.* The preceding monolayer structure represents one extreme. The other extreme form is that where the molecules on the average stand upright on the liquid surface (i.e. the long axis of the molecule is nearly perpendicular to the liquid surface). Molecules that form such monolayers are, for instance, those with one polar or a few polar groups

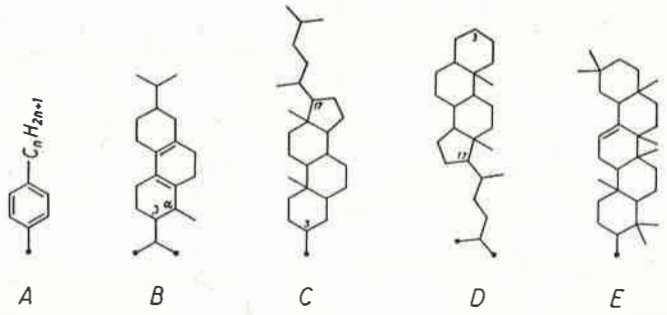



*Fig. 2, A—E.* Structures of molecules that assume on average a vertical position on an aqueous substrate. Oxygen atoms and hydroxyl groups are indicated by black circles.

A Para-alkylphenols (n = 16, 18),
B Retenecarboxylic acids with the carboxyl group in the β-position (decahydroretene-β-carboxylic acid),
C Tetracyclic compounds related to sterol (cholestan-3-ol),
D Bile acids of the cholanic acid type (cholanic acid),
E Pentacyclic compounds (β-amyrine),

at one end of the molecule. Compounds of this type are certain para-alkylphenols [16] (Fig. 2, A), various retenecarboxylic acids with a carboxylic group in the β-position [17,18] (B), many tetracyclic compounds related to sterol such as cholestan-3-ol [19] (C), bile acids of the cholanic acid type [20] (D) and pentacyclic compounds such as β-amyrine [21] (E).

Most compounds of the latter type form condensed monolayer phases. The molecules in these monolayers are more or less firmly bound to one another by strong cohesive forces between the molecules. When the area available is larger than that taken up by adjoining monolayer-forming molecules, monolayer islands are formed on the substrate surface. The uncovered liquid surface between these islands is occupied by single or small groups of molecules, whose number is determined by the two-dimensional vapour pressure of the monolayer compound. This two-dimensional vapour pressure varies from compound to compound.

*Variable Monolayer Structures.* A great majority of the compounds that form monolayers form films whose structures are highly sensitive to variations in the environmental conditions, especially to variations in the available phase boundary area. Depending on the conditions, the monolayers may consist of lying, sloping, or upright molecules. When the molecules are flexible or branched, they may be bent in a varying degree in the monolayer.

Compounds that form layer structures that vary with the magnitude of the liquid area available are the *linear* and



*branched long-chain acids, alcohols, esters* and other long-chain compounds. When the available area is large, several of these compounds have been found to form layers of horizontal molecules. When the monolayer is compressed to a smaller area, the cohesive forces between the monolayer molecules begin to operate. Groups of molecules with their hydrocarbon chains in contact with one another are formed. Further compression of the monolayer leads to a denser packing of upright molecules. The highest degree of packing occurs when this packing corresponds to that in a three-dimensional crystal. This degree of packing exists in monolayers of, e.g., palmitic, stearic and behenic acids when the surface pressure is 20—30 dynes per square centimetre. The area occupied by the molecule is then between 19 and 20 square angstroms, which is nearly the same as the cross-sectional area of the molecules in crystals of these fatty acids.

Phase and structural transitions often take place when monolayers of long-chain compounds are compressed. These will be discussed in the next lecture (M. Lundquist).

Of considerable interest is the fact that the arrangement and density of packing of the molecules in a film may influence the reactivity of the monolayer substance with compounds in adjoining media. The rates of reaction may vary greatly with the degree of compression of the monolayer. Thus, for example, the rate constant of lactone formation by γ-hydroxystearic acid spread on hydrochloric acid is about $12 \cdot 10^{-2}$ l/mole·min at a surface pressure of 8 dyne/cm, but only about $6 \cdot 10^{-2}$ l/mole·min at a surface pressure of 16 dyne/cm. The reason may be that the hydroxyl groups are less likely to form lactone rings when the molecules are forced closer to one another [22].

Also a monolayer of the unsaturated brassidic acid reacts less readily with an underlying 0.005 per cent potassium permanganate solution when its molecules in the monolayer become more densely packed. The molecules undergo oxidation readily when the surface pressure is low, but when the latter exceeds 8 dynes per centimetre, practically no reaction at all occurs [23].

Cases are also known where an increased compression promotes reactivity. An example is the hydrolysis of an ester formed by a long-chain alcohol and a fatty acid on an alkaline substrate. The greater reactivity may result from the fact that on compression functional groups in the monolayer substance are turned into a position more favourable for interaction with the solute in the substrate [24,25].

Compared with the long-chain compounds which exhibit the greatest variations in their monolayer structures, compounds with *rigid molecules* form monolayers that undergo much less change on compression. In their monolayers the molecules of the latter compounds may assume an inclined position that takes

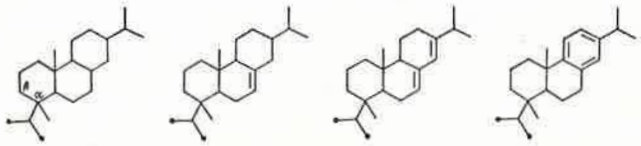



*Fig. 3, A—D.* Examples of molecules with rigid structures which undergo only slight changes in inclination on compression of their monolayers. Oxygen atoms and hydroxyl groups are indicated by black circles.

A Tetrahydroabietic acid,
B Dihydroabietic acid,
C Abietic acid,
D Dehydroabietic acid.

less space on compression. This is illustrated by the behaviour of the abietic acids (Fig. 3). Owing to the position of the carboxyl group relative to the long axis of the molecule (the $\alpha$-position (see Fig. 3 A), as compared with the $\beta$-position in retenecarboxylic acid (see Fig. 2 B)), the molecules assume an inclined position in the uncompressed monolayer (the angle formed with the water surface is of the order of 70—80°). Compression of the monolayer or a reaction between abietic acid and aluminium ions in the substrate to give aluminium abietate causes the molecules to take up a more vertical position in the monolayer [26–28].

A significant observation in this connection is that the presence of double bonds in the abietic acid skeleton alters the areas occupied by the molecules in uncompressed monolayers. The area per molecule increases with the number of double bonds in the series tetrahydroabietic, dihydroabietic, 1-abietic and dehydroabietic acid (Fig. 3 A, B, C and D), evidently owing to the slightly different inclinations of the molecules relative to the substrate surface. The monolayer structure is hence sensitive to relatively small changes in molecular structure [26–28].

*

Owing to these simple molecular relationships and the sensitivity with which the properties of monolayers change with the molecular structure of the compounds they are composed of, the monolayer represents a state of matter which is eminently suitable for the study of various types of interactions between molecules and the part played by steric factors in these interactions. The clarification of these questions is of particular interest as an important step forward in the development of our understanding of the chemistry of phase boundaries in multicomponent systems. These multicomponent systems are related to those where heterogeneous reactions take place and which are so difficult to investigate, but which are encountered in numerous natural and industrial processes.



## Reviews and Monographs

*Adam, N. K.* The Physics and Chemistry of Surfaces, London 1941.
*Adamson, A. W.* Physical Chemistry of Surfaces, New York and London 1960.
*Alexander, A. E.* and *Johanson, P.* Colloid Science, Vol. 1, Oxford 1949.
*Bikerman, J. J.* Surface Chemistry, New York 1958.
*Danielli, J. F., Pankhurst, K. G. A.* and *Riddiford, A. E.* Surface Phenomena in Chemistry and Biology, London 1958.
*Davies, J. T.* and *Rideal, E. K.* Interfacial Phenomena, New York and London 1961.
*Durham, K.* Surface Activity and Detergency, London 1961.
*Gregg, S. J.* The Surface Chemistry of Solids, London 1961.
*Harkins, W. D.* The Physical Chemistry of Surface Films, New York 1952.
*Jirgensons, B.* Organic Colloids, Amsterdam and New York, 1958.
*Rosen, M. J.* and *Goldschmidt, H. A.* Systematic Analysis of Surface-Active Agents, New York, London, 1960.
*Schwartz, A. M.* and *Perry, J. W.* Surface Active Agents, Their Chemistry and Technology, New York and London, 1949.
*Schwartz, A. M., Perry, J. W.* and *Berch, J.* Surface Active Agents and Detergents, Vol. 2, New York and London, 1958.
*Schönfeldt, N.* Oberflächenaktive Anlagerungsprodukte des Äthylenoxyds, ihre Herstellung, Eigenschaften und Anwendung, Stuttgart, 1959.
*Stenhagen, E.* Surface Films in Brady and Nachod. Determination of Organic Structures by Physical Methods, New York and London, 1955, p. 300.
*Trurnit, H. J.* Über monomolekurare Filme an Wassergrenzflächen und über Schichtfilme. Fortschritte der Chemie organischer Naturstoffe, IV Band, 1945, pp. 347—475.

## References

1. *Bruun, H. H.* Acta Acad. Aboensis, Math. et Phys. *22* (1961) 5.
2. *Adam, N. K.* Proc. Roy. Soc. (London) *A 119* (1928) 635.
3. *Adam, N. K.* Proc. Roy. Soc. (London) *A 119* (1928) 639.
4. *Ekwall, P., Ekholm, R.* and *Norman, A.* Acta Chem. Scand. *11* (1957) 703.
5. *Adam, N. K., Danielli, J. F., Haslewood, G. A. D.* and *Marrian, G. F.* Biochem, J. *26* (1932) 1233.
6. *Adam, N. K.* and *Jessop, G.* Proc. Roy. Soc. (London) *A 112* (1926) 376.
7. *Hughes, A., Schulman, J.* and *Rideal, E. K.* Nature *129* (1932) 21.
8. *Hughes, A. H.* and *Rideal, E. K.* Proc. Roy. Soc. (London) *A 137* (1932) 62.
9. *Hughes, A. H.* Trans. Far. Soc. (London) *29* (1933) 211.
10. *Fosbinder, R. J.* and *Lessig, A.* J. Franklin Inst. *215* (1933) 579.
11. *Neurath, H.* and *Bull, H. B.* Chem. Reviews *23* (1938) 391.
12. *Moss, S. A.* J. Am. Chem. Soc. *56* (1934) 41.
13. *Katz, J. R.* and *Samwel, P. J. P.* Justus Liebigs Ann. Chem. *472* (1929) 241.
14. *Adam, N. K.* Trans. Far. Soc. *29* (1933) 90.
15. *Harding, J. B.* and *Adam, N. K.* Trans. Far. Soc. *29* (1933) 837.
16. *Adam, N. K.* Proc. Roy. Soc. (London) *A 103* (1923) 676.
17. *Ekwall, P.* Svensk Kem. Tidsk. *63* (1951) 277.
18. *Ekwall, P.* Kolloid-Z. *125* (1952) 129.
19. *Adam, N. K., Askew, F. A.* and *Danielli, J. F.* Biochem. J. *29* (1935) 1786.
20. *Ekwall, P., Ekholm, R.* and *Norman, A.* Acta Chem. Scand. *11* (1957) 693.
21. *Askew, F. A.* J. Chem. Soc. *1936*, 1585.
22. *Davis, J. T.* Trans. Far. Soc. *45* (1949) 448.
23. *Rideal, E. K.* Surface Chemistry, New York 1950, p. 69.
24. *Alexander, A. E.* and *Schulman, J. H.* Proc. Roy. Soc. (London) *A 161* (1937) 115.
25. *Alexander, A. E.* and *Rideal, E. K.* Proc. Roy. Soc. *A 163* (1937) 70.
26. *Bruun, H. H.* Acta Chem. Scand. *6* (1952) 494.
27. *Bruun, H. H.* Surface Balance Studies of Rosin Acid Monolayers. Acta Acad. Aboensis, Math. et Phys. *19* (1954).
28. *Bruun, H. H.* Finska Kemistsamf. Medd. *63* (1954) 22.

FINSKA KEMISTS. MEDD. 72 N:o 1 (1963) SUOMEN KEMISTIS. TIED.

# Condensed Phases in Insoluble Monomolecular Films on Water

*Monica Lundquist*

*Institute of Medical Biochemistry, University of Göteborg.*

Monomolecular films show several well-defined surface phases, which from certain points of view are analogous to the phases found in ordinary three-dimensional systems: the gas phase, and liquid and solid phases of different structures. As no methods are available for a direct study of molecular structure in surface films on a liquid substrate, conclusions about the molecular arrangement must be drawn in a more indirect way. Langmuir's study in 1917 of monolayers of normal fatty acids (1) may be mentioned as an example of the earlier monolayer investigations. He showed that the area occupied by one molecule at the limiting area of the monolayer is independent of the chain length. Knowing the diameter of the carbon atom, Langmuir concluded that fatty acid surface films consist of monomolecular layers, where zig-zag hydrocarbon chains are standing vertically in the surface and are anchored in the substrate by the hydrophilic carboxylic acid heads.

The following survey will be limited to an account of condensed phases in monolayers of long chain aliphatic compounds with small polar groups, such as fatty acids, alcohols and esters. Besides the gas phase these compounds form several liquid and solid condensed phases. In several cases conclusions about molecular structure in these phases have been drawn from indirect evidence. Some investigations on condensed phases in monolayers of aliphatic compounds with very long chains have been carried out at the Institute of Medical Biochemistry in Göteborg.



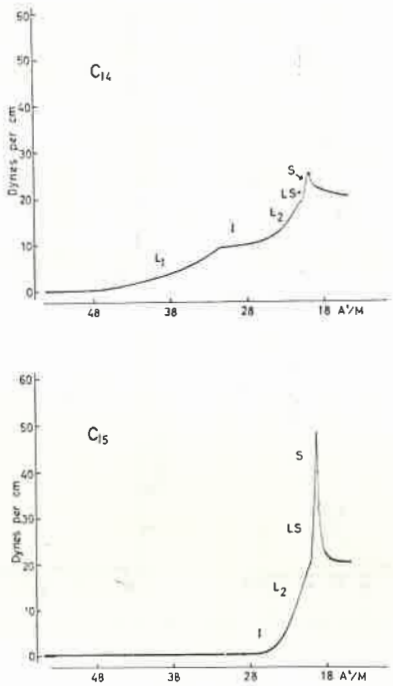



*Fig. 1.* $\pi$-A isotherms for straight-chain fatty acids in the undissociated state on 0.01 N HCl at 15°.

In a series of homologous compounds the different phases exist in different temperature regions depending on the chain length. A lowering of the temperature by 5° has about the same effect as an increase of the chain length by one methylene group. Figs. 1—3 show a series of $\pi$—A isotherms for straight chain fatty acids of increasing chain length in the undissociated state (pH in the substrate = 2). The $\pi$—A curves were all obtained at a temperature of 15°. A surface balance of the horizontal Langmuir-Adam type was used. The isotherms were continually registered by the mikrokator method (2).

The $\pi$—A isotherm for myristic acid is shown in Fig. 1 ($C_{14}$). The plateau at areas larger than 48 Å²/molecule corresponds to a pressure of only some tenths of a dyne per cm. It represents an ordinary phase transformation from the gas phase to a condensed liquid phase with a limiting area of 48 Å²/molecule. This phase is denoted $L_1$ by Harkins (3) or called *liquid expanded* by Adam (4), and corresponds to the liquid state in three dimensions. At an area of 32 Å²/molecule and a pressure of 9 dynes/cm a kink in the curve marks the beginning of a transformation, denoted by I, *intermediary phase*, to another liquid phase having

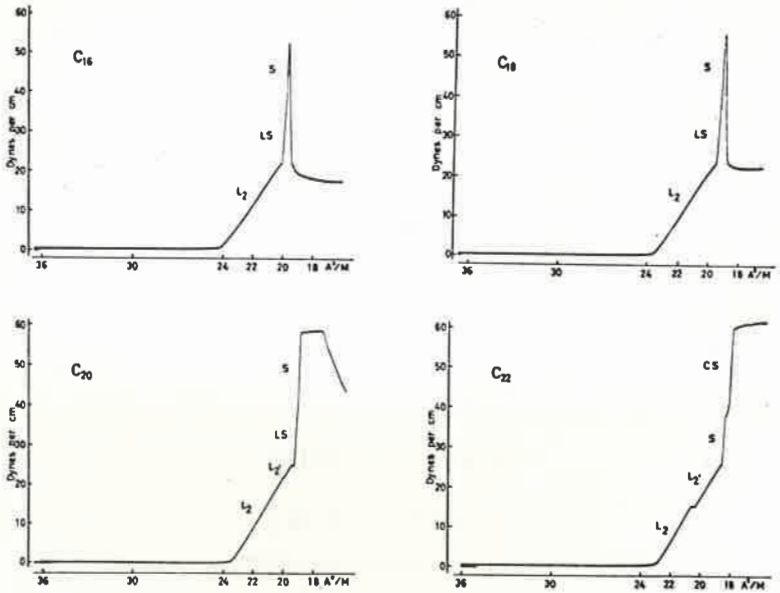



*Fig. 2.* $\pi$-A isotherms for straight-chain fatty acids in the undissociated state on 0.01 N HCl at 15°.

considerably lower compressibility, the $L_2$ phase (Harkins) or the *liquid condensed phase* (Adam). At 19 dynes/cm there is a kink in the curve after which the compressibility becomes relatively much smaller and the pressure rapidly rises. The monolayer is now solid. At an area of 20.1 Å²/molecule and a pressure of 25 dynes/cm a collapse to three-dimensional aggregates takes place. The steep part of the curve represents obviously a state in which the molecules are oriented vertically in the surface. A close examination of the steep part of the curve reveals one more kink between two phases of somewhat different compressibility. The one with the largest compressibility corresponds to the LS phase, *super liquid* according to Harkins, and the other to the S phase, the *solid* phase.

An increase of the chain length by one carbon atom ($C_{15}$, Fig. 1) causes the $L_1$ phase to disappear completely, and the gas phase condenses almost directly to the $L_2$ phase. The phases $L_2$, LS and S are separated by abrupt changes in compressibility without any simultaneous discontinuity of the area.

Palmitic and stearic acids ($C_{16}$ and $C_{18}$, Fig. 2) show likewise the phases $L_2$, LS and S. At a chain length of twenty carbon atoms, n-eicosanoic acid ($C_{20}$, Fig. 2), there appears one more phase with a rather high compressibility, the so-called $L_2$' phase according to Ställberg-Stenhagen and Stenhagen (5, 6).



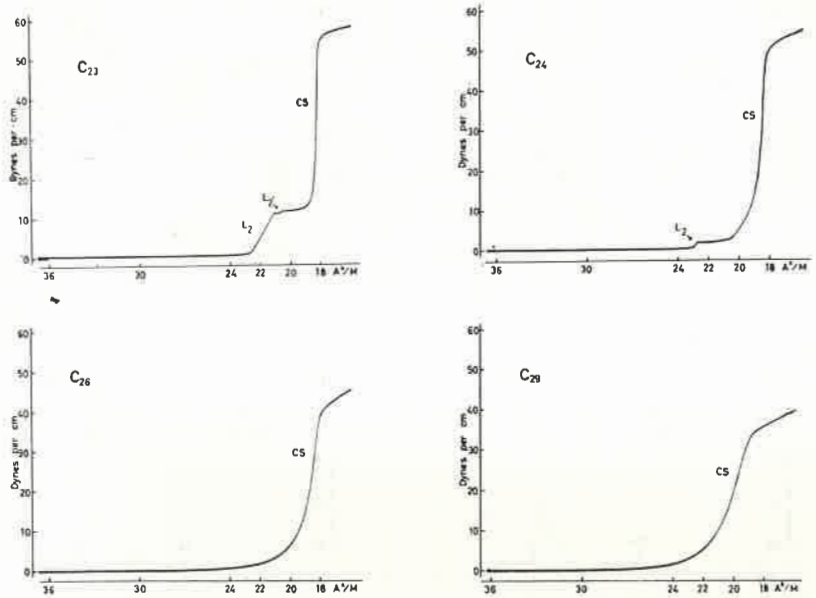



*Fig. 3.* $\pi$-A isotherms for straight-chain fatty acids in the undissociated state on 0.01 N HCl at 15°.

The two $L_2$ phases are separated by a small plateau in the $\pi$-A curve, corresponding to a first-order phase transformation, at a pressure of 22 dynes/cm. The $L_2$' phase passes over to the LS phase by an ordinary phase transformation. Both the $L_2$ and the $L_2$' phases are solid at this chain length.

For n-docosanoic acid with 22 carbon atoms ($C_{22}$, Fig. 2) the transformation $L_2$—$L_2$' takes place already at a pressure of 15 dynes/cm. At this chain length the LS phase has disappeared and a transformation to the S phase takes place directly from the $L_2$' phase. At a pressure of 38 dynes/cm, there appears one more phase transformation to the so-called CS phase, *close packed solid*, according to Ställberg-Stenhagen and Stenhagen (5, 6). At a temperature of 15°, n-docosanoic acid is the shortest fatty acid that shows the CS phase. The molecular area in the CS phase is the smallest area ever found for long chain aliphatic compounds. Collapse takes place at an area of 18,1 Å²/molecule. Extrapolated to zero pressure the molecular area in the CS phase is 18.5 Å²/molecule.

A lengthening of the chain by one more carbon atom to obtain n-tricosanoic acid ($C_{23}$, Fig. 3) causes the S phase to disappear, and a transformation from the $L_2$' phase to the CS phase takes place at a pressure of 11 dynes/cm. With n-tetracosanoic acid ($C_{24}$, Fig. 3) a condensation to the CS phase from the $L_2$ phase

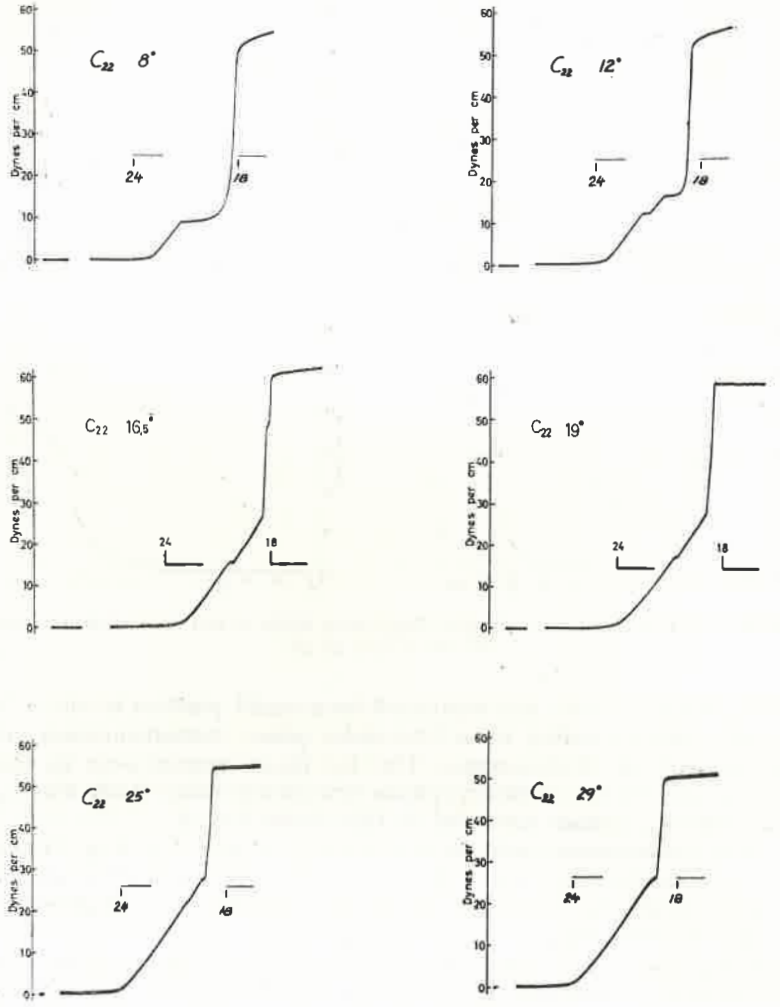



*Fig. 4.* $\pi$-A isotherms for n-docosanoic acid in the undissociated state on 0.01 N HCl at different temperatures.

takes place already at a very low pressure. With fatty acids with still longer hydrocarbon chains no $L_2$ phases will be formed and there will be a direct condensation from the gas phase to the CS phase as shown for n-hexacosanoic acid and n-nonacosanoic acid ($C_{26}$ and $C_{29}$, Fig. 3). At this chain length the monolayers are exceptionally rigid. A compressed monolayer of n-nonacosanoic acid lies as a skin on the surface for a rather long time even when the limiting barrier has been removed and the monolayer has the possibility of expanding freely.



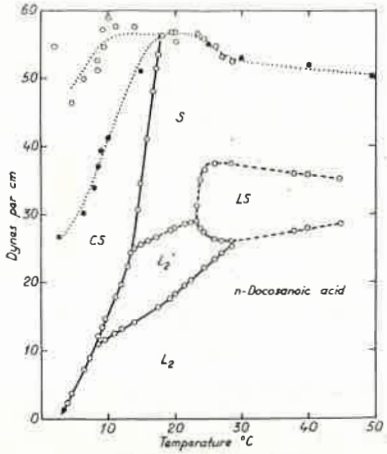



*Fig. 5.* $\pi$-T diagram for n-docosanoic acid on 0.01 N HCl. (After Ställberg-Stenhagen and Stenhagen (7).)

The smallest molecular area occupied by a long chain aliphatic compound is thus 18.3—18.5 Å² for the CS phase at zero pressure in a monolayer of n-docosanoic acid. The corresponding values for the S phase and the $L_2$ phase of n-docosanoic acid are respectively 19 and 23 Å²/molecule at 15°. Shorter homologues occupy larger areas. The areas increase by a factor of about 0.2 Å² per carbon atom with diminishing chain length.

A monolayer of a fatty acid of defined chain length will show the various phases and phase transformations when the temperature is altered in the appropriate way. As was mentioned above, a lowering of the temperature has the same effect as a lengthening of the hydrocarbon chain.

A series of $\pi$-A isotherms for n-docosanoic acid at different temperatures is shown in Fig. 4. At very low temperatures, e.g. at 2°, the gas phase condenses directly to the CS phase. At 8° the $L_2$ phase has appeared. At 12° also the $L_2'$ phase is present and the transformation to the CS phase takes place at a higher pressure. At 16.5° the isotherm shows the same general appearance as at 15° ($C_{22}$, Fig. 2). $L_2$, $L_2'$, S and CS phases are present. The S—CS transformation, however, takes place at a higher pressure. At 19° the CS phase has disappeared. The pressure for the transformation $L_2$—$L_2'$ rises with temperature, and only the $L_2$, LS and S phases are present at 29°.

Fig. 5 shows a phase diagram for n-docosanoic acid where the pressures for the different phase transformations are plotted against temperature. Ordinary changes of phase, characterized by plateaus in the $\pi$-A curves, are represented by solid lines, whilst transformations characterized by changes in compressi-

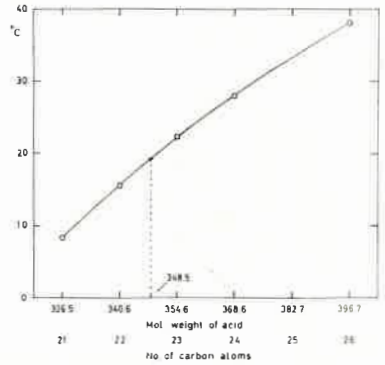



*Fig. 6.* The temperature at which the CS—S phase transformation occurs at a pressure of 38 dynes/cm for straight-chain fatty acids in the undissociated state on 0.01 N HCl *versus* chain length (molecular weight). (After Bergström, Ryhage and Stenhagen (8).)

bility only are represented by dashed lines. The dotted curve shows the collapse pressure. The regions of existence of the different phases are clearly shown: the CS phase at low temperatures, the $L_2$, S and LS phases at higher temperatures, and the very limited region for the $L_2$' phase. The presence of four triple points is to be noted. In the temperature range investigated, the $L_1$ phase is not present. It would be expected to appear at much higher temperatures.

Fig. 6 shows the increase in temperature with chain length (molecular weight) for the CS—S transformation. The temperature at which the transformation takes place at a pressure of 38 dynes/cm is plotted in the diagram. For mixtures of acids with different chain lengths the CS—S transformation will fall on this curve as a function of the mean molecular weight if the difference in the chain lengths of the compounds is not too large (8).

In the following a brief account will be given of condensed phases in monolayers of long chain alcohols and esters.

The phase diagram of n-docosanol-1 (Fig. 7) shows the presence of the high pressure phases CS, S and LS. The molecular areas for these phases agree with the areas for the corresponding fatty acid phases. The phase transformations take place at somewhat higher temperatures than those observed for the corresponding acid; for n-docosanol-1 at temperatures about 5° higher than for n-docosanoic acid. The alcohols show the presence of only one $L_2$ phase, which has a considerably smaller area than in the case of the fatty acids. For n-docosanol-1, the limiting area of the $L_2$ phase is 21 Å²/molecule at 20°.

Fig. 8 shows the phase diagrams of some esters, on one hand esters of a long chain acid, n-docosanoic acid, and short chain



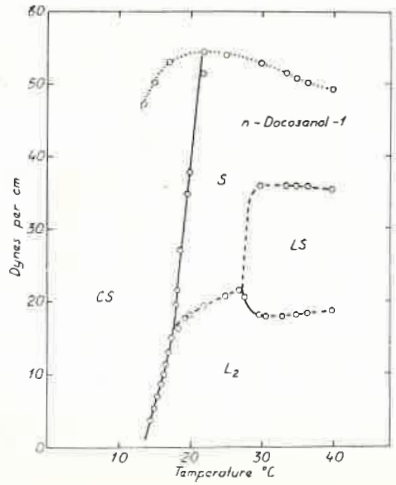



*Fig. 7.* $\pi$-T diagram for n-docosanol-1 on 0.01 N HCl. (After Stenhagen (6).)

alcohols (methyl n-docosanoate and ethyl n-docosanoate), on the other esters of a long chain alcohol, n-docosanol-1, and short chain acids (n-docosyl formate and n-docosyl acetate). All the esters mentioned form condensed monolayers with $L_2$, CS, S and LS phases. If an ester shall be able to form these very condensed monolayers where the molecules are vertically oriented in the surface, it is a necessary condition that one of the alkyl chains is not too long for otherwise a liquid expanded monolayer will be formed. n-Docosyl heptanoate, with seven carbon atoms in the chain, however, will form a condensed monolayer. The methyl and ethyl esters of n-docosanoic acid show only one $L_2$ phase, which has a limiting area of about 21 Å²/molecule. n-Docosyl formate and n-docosyl acetate, on the other hand, show both the $L_2$ and $L_2$' phases, but n-docosyl propionate shows only the $L_2$ phase. Obviously, the existence of a $L_2$' phase is determined by the molecular structure in a very subtle way.

The theory of the molecular mechanism of phase transformations in monolayers has been discussed by Joly and Dervichian (9, 10, 11). They have shown that the thermodynamic classification of transformations introduced by Ehrenfest for ordinary bulk systems is applicable to the transformations in monolayers, provided that a term for the surface energy is included in the Gibbs thermodynamic potential G:

$$G = E - TS + pV + \pi A;$$

An ordinary change of state, characterized by a plateau in the $\pi$-A isotherm, is said to be a first-order transformation, since it

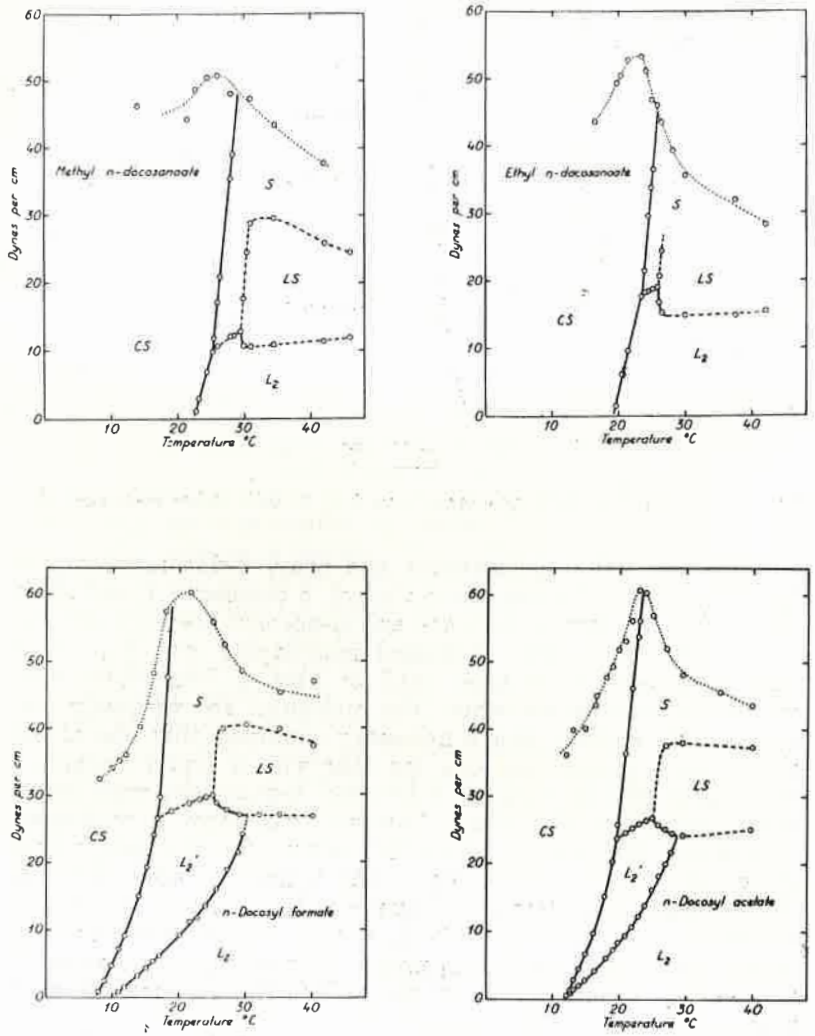



*Fig. 8.* $\pi$-T diagrams for different long-chain esters on 0.01 N HCl. (After Stenhagen (6).)

corresponds to a discontinuity of the molecular area, A, and therefore of the first partial derivative of G:

$$\left(\frac{\delta G}{\delta \pi}\right)_{p,T} = A;$$

Ordinary changes of state correspond to the equilibrium between two immiscible phases.



A sudden change in the compressibility, K, without any discontinuity of the area, corresponds to a discontinuity of the second partial derivative of G, and is called a second-order transformation:

$$\left(\frac{\delta^2 G}{\delta \pi^2}\right)_{p,T} = \frac{\delta A}{\delta \pi};$$

$$K = -\frac{1}{A} \cdot \frac{\delta A}{\delta \pi};$$

In ordinary bulk systems, a point of transformation of second order corresponds to the end of a homogeneous transformation (12). In monolayers all points of transformation would analogously correspond to the end or to the beginning of homogeneous or heterogeneous transformations. Phase transformations of still higher orders are also known to occur in monolayers.

All observed kinks in a $\pi$-A isotherm would thus correspond to the beginning or to the end of a phase transformation. The preceding considerations led Joly to make the following conclusion. The molecules in a monolayer can only exist in a finite number of stable equilibrium states, corresponding to a discontinuous series of energy states which correspond to certain characteristic areas. These areas are just the transformation points of different orders.

There has been much speculation about the molecular structure in different surface phases. In the case of solid phases a crystalline arrangement of the molecules would be conceivable, and the question arises whether there is a regular "two-dimensional" crystalline structure in these phases, or whether the structure is completely unorganized, amorphous.

The molecular areas of the phases CS, S and LS seem to be rather independent of the nature of the polar group, if it is not too large. The conclusion has been drawn that these phases represent different modes of packing of the hydrocarbon chains. In all these phases, the molecular area is so small that the molecules must be vertically oriented in the water surface. Stenhagen (6) has suggested that the chain-packing in the CS phase corresponds to the orthorombic three-dimensional form of n-hydrocarbons, since the molecular area, 18.3—18.5 Å$^2$, is just the same as the cross section of the chains in the crystalline state in question. The S phase would correspond to the $\alpha$-form, which is present just below the melting points of n-hydrocarbons and certain derivatives. The molecular packing in the $\alpha$-form is hexagonal, and the thermal effect is large, possibly so large that the chains are rotating. The molecular area in the LS phase is only slightly larger than in the S phase. Harkins called this phase *super liquid* since, for long chain alcohols, he was able to show that the viscosity of this phase is abnormally low over

a certain temperature range (13). Because of the small molecular area it must be assumed that the molecules are vertically oriented and that they probably are free to undergo both rotation and translation.

Following Joly, the $L_2$ phases must be considered as composed of molecules in two different equilibrium states, with one form passing over to the other during compression of the monolayer. At the limiting area of the $L_2$ phase, all the molecules must be present in one equilibrium state. The molecular area at this point is too large for the molecules to be vertically oriented. If the hydrocarbon chains are sufficiently long, the $L_2$ phases are solid. If there is a crystalline structure in these phases, the molecules would make an angle with the water surface. However, lower homologous compounds with the same molecular areas are liquid. The liquid $L_2$ phases may perhaps be considered as two-dimensional analogues of liquid crystals.

Dervichian has suggested that the chains in condensed phases with large areas are helically coiled (14). Depending upon the molecular area, a larger or smaller part of the chain will participate in the helix formation. In the three-dimensional state, however, the formation of helices in hydrocarbons has not been proved with certainty. It is also difficult to estimate the role played by water molecules, possibly bound by hydrogen bonds to the film-forming molecules, in forming these large-area condensed phases.

The question is whether there is an ordered structure or not in large-area condensed phases. As an attempt to study this matter, an investigation has been performed on monolayer phases of optically active and racemic forms of long chain aliphatic compounds with an asymmetric carbon atom adjoining the polar group. In the three-dimensional state, optically active and racemic forms have different crystalline structures. On the other hand, there is no difference between the forms in unorganized states, or when the molecules are rotating (15).

The structural formulas in Fig. 9 show the configurations at the polar ends of the compounds, the acetate of n-tetracosanol-2 (I) and the methyl ester of 2-methylhexacosanoic acid (II), used in these experiments. The only difference in structure between these two compounds, apart from the chain length, is the reversed location of the carbonyl group and the other ester oxygen. The presence of the methyl side group in the long chain ester molecule causes one more solid phase to appear at low temperatures. The molecular area in this phase is about 30 Å² for the optically active forms and about 28 Å² for the racemic forms. Even apart from the molecular area, this phase shows a different behaviour for the optically active and the racemic forms of the acetate and the methyl ester.



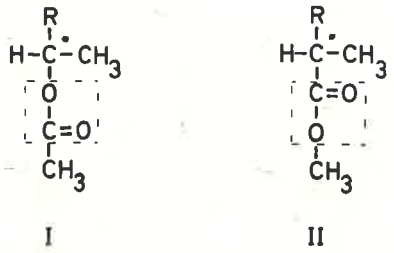



*Fig. 9.* The configuration at the polar end of the acetate of n-tetracosanol-2 (I), and the methyl ester of 2-methylhexacosanoic acid (II).

Fig. 10 shows the phase diagrams for optically active (Ia) and racemic (Ib) acetate of n-tetracosanol-2. A very beautiful, reversible, first-order transformation is observed between the low-temperature large-area phase and the CS phase. The transformation is accompanied by considerable hysteresis and the shadowed region of the diagrams represents the region of unstable pressure at a compression rate of 4 Å²/molecule/minute. The lower row of triangles connected by a full-drawn line shows the variation of the stable equilibrium pressure with temperature. The equilibrium pressure is much lower for the racemic form, and the work needed to effect transfer to the CS phase is less for the racemic acetate than for the optically active form.

The $\pi$-A isotherms of the optically active methyl esters of 2-methylhexacosanoic acid show the same general appearance as the optically active acetates. The pressure for the reversible phase transformation from the large area phase to the CS phase decreases with temperature (Fig. 10, IIa). In the case of the racemic form, the large-area phase is metastable, and a spontaneous transformation to the CS phase takes place. Consequently no stable transformation pressure is registered (Fig. 10, IIb). The phases CS, S, LS, $L_2$ and $L_2$' do not show any significant differences between the optically active and racemic forms either in the case of the acetates or in the case of the methyl esters.

Fig. 10, IIIa, shows the phase diagram for an equimolar mixture of acetate and methyl ester with the same configuration at the asymmetric carbon atom. Fig. 10, IIIb, shows the phase diagram for an equimolar mixture of acetate and methyl ester with opposite configurations, that is, a quasiracemic mixture. The $\pi$-A isotherms for the mixture of components of the same configuration show the same general behaviour as the pure optically active forms of the acetate and the methyl ester. The limiting area is about 30 Å² and a reversible first-order transformation to the CS phase is observed. The quasiracemic mixture, in conformity to the racemic forms, has a limiting area about

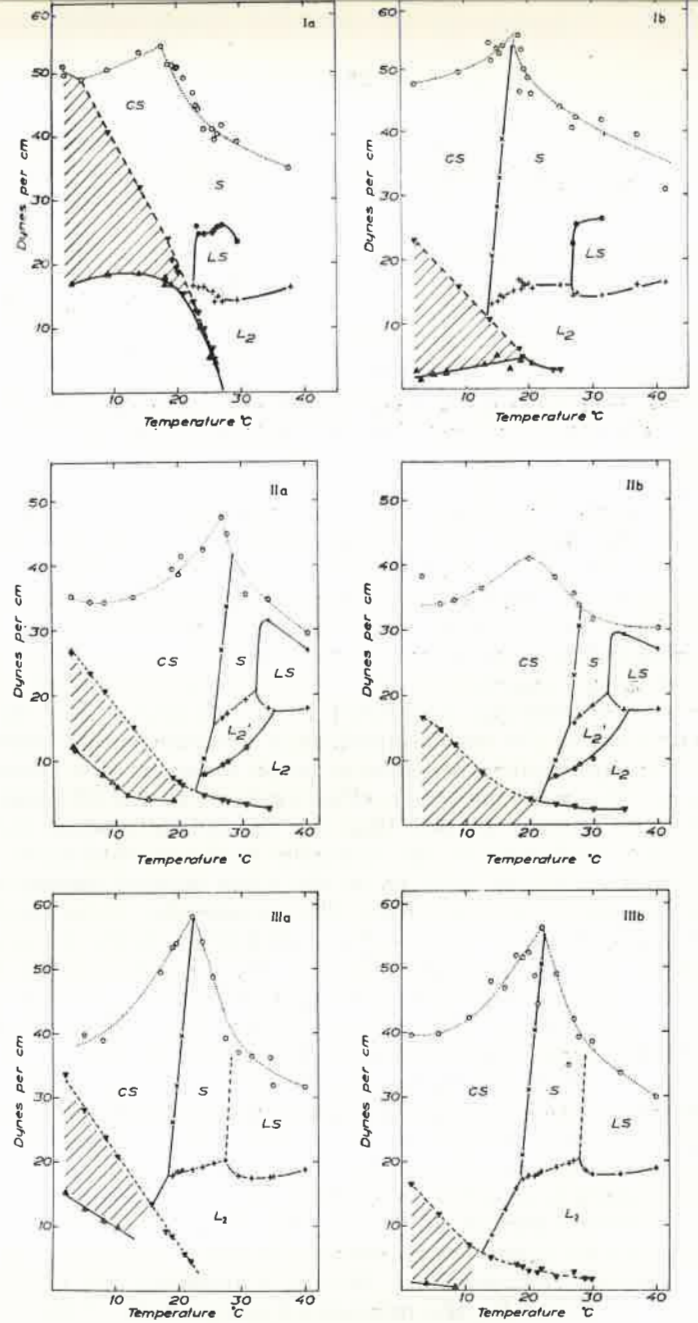



*Fig. 10.* $\pi$-T diagrams for optically active and racemic esters on 0.01 N HCl.
Ia: Optically active form of the acetate of n-tetracosanol-2.
Ib: Racemic form of the acetate of n-tetracosanol-2.
IIa: Optically active form of the methyl ester of 2-methylhexacosanoic acid.
IIb: Racemic form of the methyl ester of 2-methylhexacosanoic acid.
IIIa: An equimolar mixture of the acetate of n-tetracosanol-2 and the methyl ester of 2-methylhexacosanoic acid with the same configuration at the asymmetric carbon atom.
IIIb: A quasiracemic mixture of the acetate of n-tetracosanol-2 and the methyl ester of 2-methylhexacosanoic acid.
(After Lundquist (16, 17).)



two Å² smaller than the optically active forms, and the transformation to the CS phase takes place at a very low pressure.

In the low-temperature large-area solid phase, the molecules of the optically active and the racemic forms thus show different molecular packings. This might indicate a different mode of arrangement in a twodimensional crystalline structure, that is, in the formation of racemic and quasiracemic compounds in two dimensions. However, it is not possible at present to state in detail how the molecules are arranged. The results obtained indicate, however, that the large-area phase studied must possess an at least to a certain extent ordered structure.

## References


1. *Langmuir, I.*, J. Amer. Chem. Soc. **39,** 1848 (1917).
2. *Ställberg-Stenhagen, S.* and *Stenhagen, E.*, Nature **159,** 814 (1947).
3. *Harkins, W. D.*, "The Physical Chemistry of Surface Films", 2nd ed., New York 1954.
4. *Adam, N. K.*, "The Physics and Chemistry of Surfaces", 3rd ed., Oxford University Press, London 1941.
5. *Ställberg-Stenhagen, S.* and *Stenhagen, E.*, Nature **156,** 239 (1945).
6. *Stenhagen, E.*, "Surface Films" *in* "Determination of Organic Structures by Physical Methods" (Braude, Nachod ed.), 325, New York 1955.
7. *Ställberg-Stenhagen, S.* and *Stenhagen, E.*, Acta Chem. Scand. **3,** 1035 (1949)
8. *Bergström, H., Ryhage, R.* and *Stenhagen, E.*, Svensk Papperstidn. **59,** 593 (1956).
9. *Dervichian, D. G.* and *Joly, M.*, J. Phys Rad. VII, **10,** 375 (1939)
10. *Joly, M.*, J. Colloid Sci. *5*, 49 (1950).
11. *Dervichian, D. G., in* "The Chemistry of Fats and other Lipids" (Holman, Lundberg, Malkin ed.), Vol. 2, p. 193, London 1954.
12. *Mayer, J. E.* and *Streeter, S. F.*, J. Chem. Phys. **7,** 1019 (1939).
13. *Harkins, W. D.* and *Copeland, L. E.*, J. Chem. Phys. **10,** 272 (1942).
14. *Dervichian, D. G., in* "Surface Chemistry", p. 47. Butterworths Scientific Publications, London 1949.
15. *Hägg, G., in* "The Svedberg 1884 30/8 1944", p. 140, Uppsala 1944.
16. *Lundquist, M.*, Ark. Kemi **17,** 183 (1961).
17. *Lundquist, M.*, to be published.

FINSKA KEMISTS. MEDD. N:o 1 **72** (1963) SUOMEN KEMISTIS. TIED.

# Fundamental Problems in the Thermodynamic and Statistical Theory of Surfaces

*Jørgen Koefoed*

*Fysisk-Kemisk Institut, Danmarks tekniske Højskole, København Ø.*

The surface systems we have been working with in Copenhagen are extremely simple. We have measured surface tension as function of the composition for two component mixtures of simple organic liquids. Some of them are published (Acta Chem. Scand. 12 (1958) 1124), most of them are still unpublished.

Our aim has been to contribute to the fundamental knowledge of surface problems by providing some material that could be compared with results of statistical theory on simple models of a liquid surface, and in this work we have been led to the conclusion that some of the established views on this matter were in need of some revision (*cf.* E. A. Guggenheim: Mixtures, O.U.P. 1952 chapter 9).

Guggenheims' expression for a monolayer model has two serious defects:

1) it leads to identical values of surface energy and surface tension,
2) it leads to expressions which are not consistent with Gibbs' adsorption theorem.

Gibbs' derivation of this theorem has often been criticised because his definitions of surface concentrations have been misunderstood, but the point which is — in my opinion — dubious, is his use of the chemical potential in the surface.

If we introduce surface area, $a$, as a parameter to supplement $S$, $V$, and $n_i$ we have altogether $k + 3$ variables, to which $k + 3$ conjugate potentials $\gamma$, $T$, $P$, $\mu_i$ can be defined in the well-known way. Two of the potentials will be redundant in the description of a system in internal equilibrium by potentials alone, and their



interdependence is expressed through the fifth fundamental equation of Gibbs:

$$0 = S\mathrm{d}T - V\mathrm{d}p + a\mathrm{d}\gamma + \Sigma n_i \mathrm{d}\mu_i$$

Now, our $\mu$'s are the chemical potentials in the bulk phase and in order to attach any meaning to a chemical potential of components in the surface we must define first a set of variables, $n_i'$, describing the amounts of chemical matter in the surface phase and conjugate to these variables we will find what we can properly call the chemical potentials $\mu_i'$, of our components in the surface phase. All these variables will be redundant in the description of equilibrium systems.

Considering next the total differential:

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \gamma\mathrm{d}a + \Sigma\mu_i \mathrm{d}n_i$$

we realize, that we cannot just add to this expression the terms $\Sigma\mu_i'\mathrm{d}n_i'$, because in order to preserve for $\mathrm{d}E$ the character of a total differential, the coefficients of each single differential term will acquire thereby a new physical meaning. It is only for the coefficient to $\mathrm{d}a$, though, that it will mean a significant change: $\gamma = (\partial E/\partial a)_{S,V,n_i}$ will be superseded by $(\partial E/\partial a)_{S,V,n,n_i'}$, just as $\mu_i'$must be defined as $(\partial E/\partial n_i')_{S,V,a,n_{i'},n_j'}$. This, of course, leads to something of a very speculative nature, since it involves processes we can have no hope of performing, as we have no possibility of changing area without changing number of molecules in the surface, nor vice versa.

The way out of this dilemma is to reduce the number of redundant parameters, so that in introducing $n_i'$ as fundamental variables we skip $a$, and write:

$$\mathrm{d}E = T\mathrm{d}S - p\mathrm{d}V + \Sigma\mu_i \mathrm{d}n_i + \Sigma\mu_i'\mathrm{d}n_i'$$

having still $k-1$ redundant extensive variables when applied to equilibrium systems. Introducing next specific surface areas:

$$a_i = (\partial a/\partial n_i')_{T,p,n_{i'},n_j'}$$

we see how the two expressions for $\mathrm{d}E$ are made to agree by the relations:

$$\mu_i' = \mu_i + a_i\gamma \quad \text{and} \quad \mathrm{d}\mu_i' = \mathrm{d}\mu_i + a_i\mathrm{d}\gamma$$

The fifth fundamental takes the form:

$$0 = S\mathrm{d}T - V\mathrm{d}p + \Sigma n_i \mathrm{d}\mu_i + \Sigma n_i'\mathrm{d}\mu_i'$$

and at constant $T$ and $p$:

$$\Sigma n_i \mathrm{d}\mu_i = 0 \quad \text{and} \quad \Sigma n_i'\mathrm{d}\mu_i' = 0$$

the latter giving directly Gibbs' adsorption theorem:

$$a\mathrm{d}\gamma + \Sigma n_i'\mathrm{d}\mu_i = 0$$

Our conclusion is, therefore, that although Gibbs in his derivation has used chemical potentials in an improper way, his result is nevertheless correct.

The fact, that the chemical potential of a component is not necessarily identical in the surface and in the bulk is a consequence of the particular kind of incomplete equilibrium which exists in a surface system. Surface exists only by force of external circumstance. Given the liberty to do so, surface area will have shrunk to zero in a state of complete equilibrium.

Another consequence will be that pressure has not necessarily the same value in surface and in bulk phase. That means that we need not think of surface tension as a twodimensional negative pressure (van der Waals and Bakker). In a liquid it is really against all general physical laws that pressure could be non-isotropic, and it is much more satisfactory to be able to consider the surface as a narrow zone in a state of isotropic, negative pressure.

If we consider as an example $CCl_4$ at 25°C, 1 atm, it has in the bulk phase an internal pressure $\pi = (\partial E/\partial V)_T$ of 3310 atm and the molar volume is 97 ml/mol. In a monolayer model we can take the thickness of the surface phase as $\tau = 5.0$ Å and the specific area $a_1 = 19.5 \cdot 10^8$ cm²/mol. $\gamma = (p - p')\,\tau = 26$ dyn/cm corresponds then to a pressure in the monolayer of $-500$ atm and the surface energy $E' = (\partial E/\partial a)_{T,p'}$ which is 65,6 dyn/cm, can be interpreted as due to a difference in internal pressure $(\pi - \pi')$ of 1300 atm giving for $\pi'$ a value of 2010 atm.

In the statistical theory of liquid surfaces we can in a monolayer quasi-crystalline model assume with Guggenheim that we can write partition functions $q_i'$ for the surface states which are related to the $q_i$ of the bulk phase states through the relation

$$kT \ln (q_i/q_i') = m\chi_i$$

when $m$ is the fraction of nearest neighbours missing in the surface states, and $\chi_i$ is the potential energy of intermolecular forces in the bulk phase.

In stead of assuming that the absolute activity $\lambda_i$ is the same in bulk and in surface, we are led to introduce:

$$kT \ln (\lambda_i/\lambda_i') = \gamma a_i$$

and we find for a pure liquid the consequences:

$$2\gamma a_i = kT \ln (q_i/q_i') = m\chi_1$$

$$E' a_i = k\partial \ln(q_i/q_i')/\partial\,(1/T) = m\chi_i$$

That surface tension comes out as half the surface energy is in very good agreement with the measurements on $CCl_4$ at 25°C as quoted above. This is, of course, a coincidence since the agreement will be less good at other temperatures. But under conditions where the quasi-crystalline model is applicable, it is usually not bad as far as order of magnitude is concerned (liquid metals excluded), and in any case it is certainly a less crude approximation than it is to have $E'$ equal to $\gamma$, as implied by Guggenheims' treatment.



Going on to mixtures we can derive a number of relations which are somewhat different from those of Guggenheim and essentially the same as those proposed in our publication (*loc.cit.*) They give as the "ideal surface behavior" of mixtures a straight line relationship between $\gamma$ and $x$, and they are inherently in accordance with Gibbs' theorem.

One particularly interesting feature is that our expressions allow us in the surface tension to distinguish between different kinds of deviations from ideality that are indistinguishable in the bulk phase properties.

A serious difficulty is that any significant comparison of model calculations with experiments require very accurate measurements of surface tension and — much worse — of surface energy.

FINSKA KEMISTS. MEDD. 72 N:o 1 (1963) SUOMEN KEMISTIS. TIED.

# Adsorption of Cholesterol at Oil – Water Interfaces

*O. Harva*

*Finland Institute of Technology, Helsinki, Finland*

Polar, oil-soluble compounds like cholesterol, fatty alcohols and monoglycerides are known to improve the properties of anionic emulsifying agents and the stability of emulsions [1]. Schulman and Cockbain [2] assumed that the polar compounds form interfacial complexes with the tensides. Studying the effect of cholesterol, cholesterol myristate and other oil-soluble compounds on the interfacial tension of 0.01 M sodium dodecyl sulphate against benzene, Alexander and Schulman [3] concluded that a decrease in the interfacial tension caused by the oil-soluble compounds would prove the existence of such interfacial complexes. This conclusion was not, however, supported by subsequent measurements of interfacial tension. Hutchinson [4], for example, was unable to detect the formation of interfacial compounds when he studied the influence of octyl alcohol on the interfacial tension between a sodium dodecyl sulphate solution and benzene. Cockbain and McMullen [5] came to the same conclusion after studying the effects of cholesterol, sitosterol and octadecanol on the interfacial tensions of sodium dodecyl sulphate and potassium laurate solutions against benzene and n-decane.

As the adsorption of cholesterol at the interface between an oil and water has not been studied quantitatively, a series of interfacial tension measurements were carried out to study this adsorption in the light of Gibbs' theory. Although it could not be expected that the results would be very accurate, it was nevertheless hoped that they would provide information about the nature of the adsorbed film and an indication of any interaction between solutes at the interface.



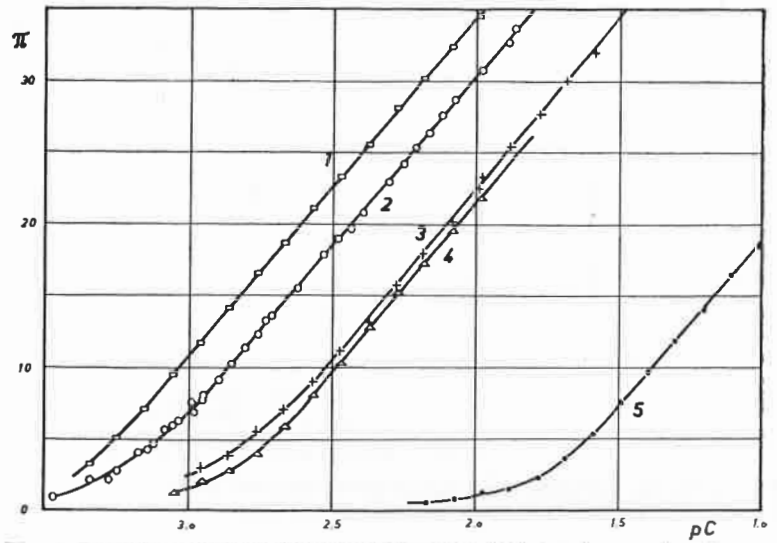



*Fig. 1.* Lowering of interfacial tension between hydrocarbons and water as a function of cholesterol concentration (25°C). Curve 1, iso-octane; curve 2, n-heptane; curve 3, cyclohexane; curve 4, di-isobutene; and curve 5, benzene.

## *Adsoption of Cholesterol at Hydrocarbon—Water Interfaces*

The interfacial tensions between solutions of cholesterol in hydrocarbons * and water at 25°C were measured by the ring method using a de Noüy tensiometer. The ring corrections were made according to Zuidema and Waters [6]. The results are seen in Fig. 1, where the ordinate is the surface pressure and the abscissa the negative logarithm of the cholesterol concentration ($pC_a$). The curves plot results obtained with different hydrocarbons. The curves rapidly become linear as the surface pressure increases. According to Gibbs' theory, this means that the amount of cholesterol that is adsorbed at the interface does not increase when a certain concentration and surface pressure is exceeded. If the activity of cholesterol is assumed equal to its molar concentration in dilute solutions, the amount of cholesterol adsorbed per unit area is given by equation

* The iso-octane and n-heptane were products of Phillips Petroleum Co. They were treated with concentrated sulphuric acid and washed with aqueous caustic soda solution and water, after which they were passed through an alumina column.

The di-isobutylene was obtained from Shell Chemical Co. and was further purified by distillation over sodium in a nitrogen atmosphere.

The benzene and cyclohexane were guaranteed reagents from E. Merck AG, Darmstadt.

The cholesterol was obtained from Difco Laboratories, Detroit. Its molecular weight as determined ebullioscopically[7] in benzene was 385 and its melting point 148.5°C (corr.).

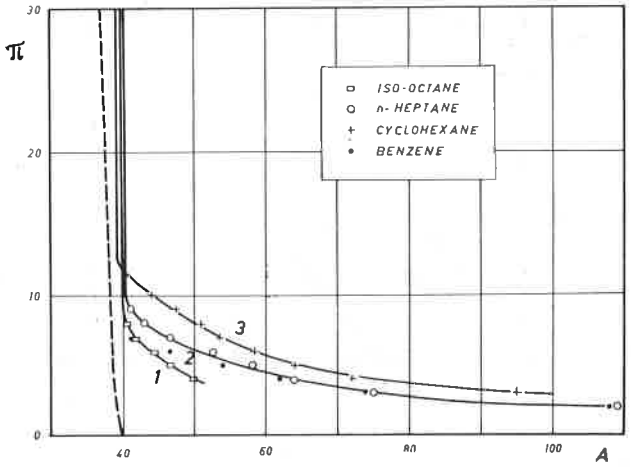



*Fig. 2.* Surface pressure-area curves for cholesterol at hydrocarbon-water interfaces.

$$n_a = -\frac{1}{2{,}303\ kT} \cdot \frac{d\pi}{d\ (pC_a)}$$

where $n_a$ is the number of molecules of cholesterol per square centimetre, k Boltzmann's constant and T the absolute temperature (°K). If the adsorbed film is a monomolecular layer, the area per molecule is

$$A = \frac{10^{16}}{n_a}\ sq \cdot Å$$

When the slopes of the $\pi$—$pC_a$ curves are known, it is possible to calculate from these equations the amounts of cholesterol adsorbed and the molecular areas at different values of the surface pressure. The values are plotted as $\pi$—A curves in Fig. 2. These curves reveal that the molecular area remains constant when a relatively low surface pressure ($> \pi_c$) is exceeded and is independent of the nature of the hydrocarbon. The dash line in Fig. 2 is the compression curve of a monolayer of cholesterol on a 3 M sodium chloride solution according to Ekwall et al.[8]

The amounts of adsorbed cholesterol ($n_a$) and the molecular areas (A) at high surface pressures ($> \pi_c$) are shown in Table 1. These values of the area seem to be independent of the solvent. The values of the area taken up by an adsorbed cholesterol molecule, 39.3—40.5 sq.Å, are in agreement with the values of the area in compressed monolayers on water: Adam [9] 40.8 sq.Å; Ekwall et al.[8] 36—40 sq.Å; and de Bernard [10] 38 sq.Å. Harkins et al.[11] have estimated the smallest cross-sectional area of a cholesterol molecule to be 37 sq.Å and Ekwall et al.[8] have



calculated for the minimum projection area of a cholesterol molecule the value 35 sq.Å. It may hence be concluded that cholesterol forms a condensed film at hydrocarbon — water interfaces. The behaviour of $\beta$-sitosterol was found to be the same at an n-heptane — water interface; the molecular area was calculated to be 36.6 sq.Å. This is a surprising result, because polar, oil-soluble compounds such as fatty alcohols and monoglycerides do not generally form condensed films at oil-water interfaces. The molecular area in the film is usually 50—100 per cent larger than the cross-sectional area of the molecule. The condensed nature of the cholesterol layer at an oil-water interface is possibly responsible for the good emulsifying properties of the compound. It would also be interesting to know whether there is any connection between this phenomenon and the physiological properties of cholesterol.

Cholesterol forms an imperfect gaseous film at oil-water interfaces at low surface pressures. The relationship between the interfacial tension and the molecular area is given by the Amagat equation

$$\pi\ (A - A_o) = x\ k\ T.$$

The values of $A_o$ and x obtained with different solvents are shown in Table 1.

*Table 1.* Adsorption of cholesterol at oil-water interfaces at 25°C.

| Oil | $n_a$ molecules/cm² | A sq.Å/molecule | $\pi c$ dyne/cm | $A_o$ | x |
|---|---|---|---|---|---|
| Iso-octane | $2.506 \cdot 10^{14}$ | 39.9 | 9 | | |
| n-Heptane | 2.47 | 40.5 | 9 | 23 | 0.40 |
| Cyclohexane | 2.55 | 39.3 | 11 | 19.8 | 0.54 |
| Di-isobutene | 2.51 | 39.8 | 8.5 | 18.5 | 0.44 |
| Benzene | 2.48 | 40.3 | 7.5 | 15.3 | 0.45 |

### *Absorption of Cholesterol at Interfaces between n-Heptane and Aqueous Sodium Dodecyl Sulphate Solutions*

The interfacial tensions between solutions of cholesterol in n-heptane and aqueous sodium dodecyl sulphate solutions were also measured *. The interfacial tensions at 25°C are plotted as a function of the cholesterol concentration in n-heptane in Fig. 3. The different curves refer to different concentrations of sodium dodecyl sulphate in the aqueous phase. The interfacial tensions are plotted as a function of the sodium dodecyl sulphate concen-

* The sodium dodecyl sulphate was a sample provided by Dr. T. G. Jones, Unilever Ltd., England. It was a pure specimen giving no surface tension minimum.

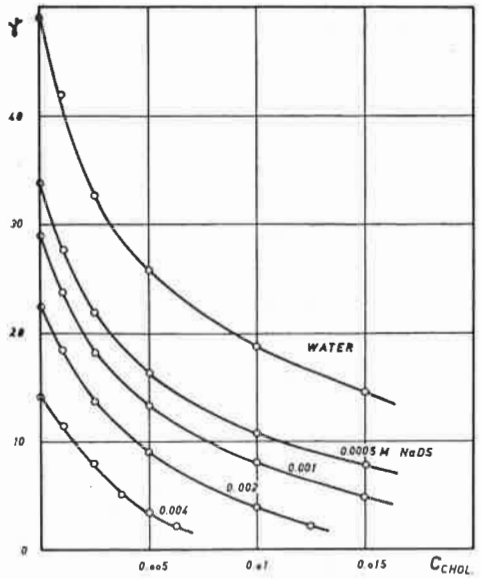



*Fig. 3.* Interfacial tension between solutions of cholesterol in n-heptane and aqueous sodium dodecyl sulphate solutions at 25°C.

tration at constant cholesterol concentration in Fig. 4. On the basis of Gibbs' theory and certain assumptions, these values can be used to calculate the amounts of the tenside (s) and cholesterol (a) at the interfaces.

According to Gibbs' theory, the change in the interfacial tension is given by

$$-\mathrm{d}\,\gamma = \Gamma_s \mathrm{d}\mu_s + \Gamma_w \mathrm{d}\mu_w + \Gamma_a \mathrm{d}\mu_a + \Gamma_o \mathrm{d}\mu_o$$

where $\gamma$ is the interfacial tension (dyne/cm), $\Gamma$ the surface excess (mole/cm$^2$) and $\mu$ the chemical potential. s denotes sodium dodecyl sulphate, w water, a cholesterol and o n-heptane.

The assumptions made are that the chemical potentials of n-heptane and cholesterol are invariant with respect to changes in the sodium dodecyl sulphate concentration and that $\Gamma_w = 0$ in accordance with Gibbs' convention. With a given concentration of cholesterol in the oil phase, the surface excess of sodium dodecyl sulphate is given by

$$\Gamma_s^1 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_s}$$

When the tenside is taken to be a completely dissociated uni-univalent electrolyte, we may write

$$\mathrm{d}\mu_s = 2\ \mathrm{RT}\ \mathrm{d}\ln a_s$$



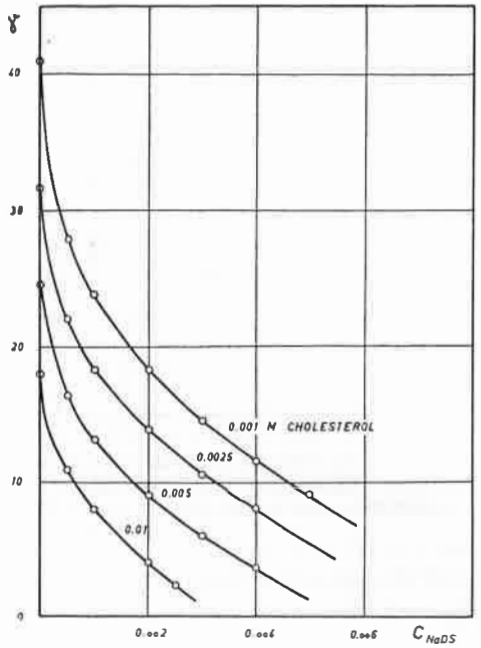



*Fig. 4.* Interfacial tension between aqueous sodium dodecyl sulphate solutions and solutions of cholesterol in n-heptane.

where $a_s$ is the mean activity of sodium dodecyl sulphate.

The mean activity of sodium dodecyl sulphate at concentrations below the critical can be calculated with sufficient accuracy from the Debye-Hückel relation

$$\log\ a_s = \log C_s - 0.5\sqrt{C_s}$$

where $C_a$ is the molar concentration of the association colloid.

The surface excess of sodium dodecyl sulphate can be calculated from

$$n_s = -\frac{1}{4.6\ \mathrm{kT}} \cdot \frac{\mathrm{d}\pi}{\mathrm{d}\ (\mathrm{pa_s})}$$

when the slope of the $\pi$—$\mathrm{pa_s}$ curve is known.

We assume further that the chemical potentials of sodium dodecyl sulphate and water do not change when the cholesterol concentration in the oil phase varies and that the surface excess of the solvent molecules [12] ($\Gamma_o$) is zero. When the concentration of sodium dodecyl sulphate in water is constant, the surface excess of cholesterol is given by

$$\Gamma_a^1 = -\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_a}$$

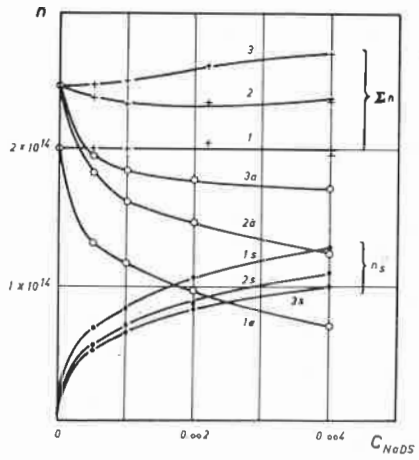



*Fig. 5.* Surface excess of cholesterol (a) and sodium dodecyl sulphate (s) at n-heptane-water interfaces. Cholesterol concentrations: 0.001 M (curves 1), 0.0025 M (curves 2) and 0.005 M (curves 3).

If the activity of cholesterol is assumed equal to its concentration, the surface excess can be calculated from the equation

$$n_a = \frac{1}{2.3\ kt} \cdot \frac{d\pi}{d(pC_a)}$$

when the slope of the $\pi - pC_a$ curve is known.

The results of the calculations are plotted in Fig. 5, where the ordinate is the surface excess of molecules and the abscissa the concentration of sodium dodecyl sulphate. The curves 1, 2 and 3 refer to 0.001, 0.0025 and 0.005 M concentrations of cholesterol in n-heptane. It is seen that as the concentration of sodium dodecyl sulphate in the aqueous phase increases, the surface excess of cholesterol decreases (curves 1a, 2a and 3a) and the surface excess of sodium dodecyl sulphate increases (curves 1s, 2s and 3s). The total amount ($\Sigma n = n_a + n_s$) of both components adsorbed does not undergo any greater variation when the bulk concentration of the surface-active agent increases, but the composition of the adsorbed film changes, a mixed film being formed whose composition depends on the concentrations of the solutes in the two liquid phases.

The curves for sodium dodecyl sulphate resemble adsorption isotherms. It was found that the amount of sodium dodecyl sulphate in the mixed film is given by the Freundlich's equation

$$n_s = K\ C_s^{\,1/\nu}$$

when $\nu = 3.23$ and the value of the constant K has a value determined by the concentration of cholesterol in the oil phase.



The amount of cholesterol in the mixed film decreases almost in the same proportion.

The results do not indicate that a complex is formed by cholesterol and sodium dodecyl sulphate at heptane-water interfaces. Sodium dodecyl sulphate is apparently able to penetrate into the condensed cholesterol film and displace cholesterol molecules to form a mixed film in which the components are not present in constant ratio and whose composition varies with the concentrations of the components in the bulk of the solutions.

## References

1. *C. Sumner*, »Clayton's theory of emulsions and their technical treatment», 5th Edition, London, 1954.
2. *J. Schulman* and *E. Cockbain*, Trans. Faraday Soc. *36* (1940) 651, 661.
3. *A. Alexander* and *J. Schulman*, Trans. Faraday Soc. *36* (1940) 960.
4. *E. Hutchinson*, J. Colloid. Sci. 3 (1948) 521.
5. *E. Cockbain* and *A. McMullen*, Trans. Faraday Soc. *47* (1951) 322.
6. *H. Zuidema* and *G. Waters*, Ind. Eng. Chem. Anal. Ed. 13 (1941) 312.
7. *C. Heitler*, Analyst 83 (1958) 223.
8. *P. Ekwall, R. Ekholm* and *A. Norman*, Acta Chem. Scand. *11* (1957) 693.
9. *N. K. Adam* and *G. Jessop*, Proc. Roy. Soc. A, 120 (1928) 473.
10. *L. de Bernard*, Bull. Soc. Chim. Biol. 40 (1958) 161.
11. *W. Harkins, H. Ries* and *E. Carman*, J. Am. Chem. Soc. *57* (1935) 2224.
12. *E. A. Guggenheim* and *N. K. Adam*, Proc. Roy. Soc. A, 139 (1933) 218.

FINSKA KEMISTS. MEDD. 72 N:o1 (1963) SUOMEN KEMISTIS. TIED.

# The Effect of Electrolytes on the Stability of Emulsions Stabilized by Anionic Soaps

*Axel O. Bohn*

*Laboratoriet for vej-og jernbanebygning samt byplanlægning, Danmarks tekniske højskole. København.*

*A. The properties of soap solutions.*

Whereas fatty acids and acetic acid are almost equally strong, the alkali metal salts of fatty acids are much more strongly hydrolyzed than the corresponding acetates. This is due to the formation of weakly dissociated, more or less soluble acid salts of the type 2NaOl,HOl and NaOl,HOl. In a 0.01 N potassium stearate solution, no less than 40 % of the soap is hydrolysed; with sodium oleate, however, the maximum degree of hydrolysis will only be 7.7 %. If an alkali metal hydroxide is added to a soap solution, the hydrolysis is suppressed, whereas an addition of fatty acid enhances the formation of acid soap. Alkyl sulphates, alkyl sulphonates and alkyl amine salts, which also exert an emulsifying action, are not hydrolysed, however.

It is characteristic of soap solutions that at and above a certain concentration (CMC, the critical micelle concentration), which for sodium oleate is about 0.001 N, the soap molecules unite to form aggregates, the so-called micelles, which in the case of sodium oleate comprise somewhat more than 100 individual molecules. At the CMC a number of properties change in a characteristic way; these are viscosity, surface tension, interfacial tension, refractive index, specific weight, heat of dilution and osmotic pressure. The existence of the micelles was established when it was noted that the osmotic pressure did not increase as expected with concentration above the CMC. The observation that the decrease of the surface and interfacial tensions of soap solutions with increasing concentration ceases at the CMC is explained by the fact that at this concentration the association of the soap molecules to micelles competes with their accumulation at surfaces and interfaces.

In a homologuous series of paraffin chain salts, the CMC decreases with increasing chainlength. At the same time, the



number of molecules in the micelles increases. The micelles have the important property of being able to solubilize organic materials which are insoluble in water. No solubilisation takes place below the CMC. When neutral and basic salts are added to a soap solution, the CMC decreases.

*B. Charge and electrophoretic velocity.*

The charges on the emulsion drops are of importance as they determine the stability of emulsions. The mean charge may be calculated from data on the electrophoretic velocity of oil drops in an electric field (electrophoresis). Powney and Wood (1) have measured the electrophoretic velocities of a drop of paraffin oil in sodium oleate solutions of different concentrations. The electrophoretic velocity of the oil drop in pure water is 4.35 $\mu$/sec. per volt/cm in the direction towards the anode in accordance with the rule laid down already in 1909 by Coehn and Raydt (2), which states that the phase with the smallest dielectric constant will be negatively charged. In sodium oleate solutions the electrophoretic velocity increases strongly at first as a consequence of the adsorption of long chain ions on the oil drop. At the concentration of 0,01 % (= 0,0003 N), a maximum near 8 $\mu$/sec. per volt/cm is recorded. The mobility then decreases a little. The authors explain this to result from a secondary adsorption of sodium ions. At the CMC the mobility increases again, which the authors explain to an increased adsorption of sodium ions as counterions to the ionised micelles. This causes a decrease of the ion concentration of the solution and the effect of sodium ion on the mobility becomes smaller. If the hydrolysis is suppressed by adding sodium hydroxide the maximum velocity is observed at lower oleate concentrations. Powney and Wood ascribe this to a suppression of the hydrolysis, but it can be supposed to be a general salt effect on the micelle formation. In both cases, the critical mobility occurs at the CMC, as determined by interfacial tension measurements.

*C. The Zeta potential.*

From the velocities of the oil drops it is possible to calculate the zeta potential S, the potential difference between the layer of liquid immediately at the surface of the particle and the liquid far away from the particle as calculated from formulae proposed by Schmoluchowski, Helmholtz and Henry (see the critical survey of Bikermann (3)).

According to Powis (4), the zeta potential must be at least 30 mV to make a suspension stable; Verwey (5) suggests that even up to 100 mV is necessary for emulsions. Eilers and Korff (6) are of the opinion, on the basis of dimensional considerations,

that $\frac{\zeta^2}{\varkappa}$, (where $\frac{1}{\varkappa}$ is Debye's average thickness of the ion sphere ($\varkappa = 10^{7.374}\sqrt{\Sigma(cz^2)}$) and where c and z are the concentration and the valency of the ions) is a better measure of stability than the zeta potential itself. On the basis of the resultant of the repulsion between the electrical double layer and the attraction between the particles as a consequence of London-van der Waal forces, Derjaguin (7), and independently Verwey and Overbeek (8), have succeeded in defining quantitatively the stability of lyophobic colloids. The theory is in agreement with Eiler and Korff's rule, and with the empirical rule laid down by Hardy and Schulze which states that the stability decreases greatly with the valence of ions with charges opposite to that of the particle. The difference between the effects of ions of equal valence is relatively small. Generally a negative sol is coagulated by large cations at a somewhat lower concentration than by small cations of the same valence (Ostwald (9)).

*D. Difference between emulsions and lyophobic colloids.*

Emulsions and lyophobic colloids differ in that emulsions normally need an emulsifier to have a fairly good storage stability. Only quite dilute emulsions and emulsions of highly polar materials such as amyl alcohol can, as shown by Cheesman and King (10), be prepared in dilute aqueous solutions of inorganic salts without adding an emulsifier. Verwey (5) states that the smallest part of the decrease in the potential takes place in the layer closest to an oil drop. Owing to the diffuse character of the two layers forming the double layer, the capacity is smaller than that at a solid-liquid interface and produces a smaller particle charge for the same double layer potential, and consequently a weaker repulsion between the particles. If emulsifiers are added, the particles resemble solid matter; the greatest potential decrease shifts to the outer phase and a greater stability results.

*E. The interfacial tension.*

In dispersions of solid matter in liquids, the interfacil tension between the dispersed phase and the dispersion medium is normally not considered in discussions of stability. However, interfacial tensions are of great importance in the case of emulsions. The interfacial tension between oil and water on addition of a soap (Hartley (11)) decreases because the water tends to force the insoluble paraffin chain of the soap molecule into the oil phase so that the interface is covered by an orientated layer of emulsifier molecules with the ionised parts of the molecules in the water phase. At the CMC the decrease in the interfacial tension ceases at a value of 1—2 dyn/cm for the straight-chain soap. The formation of micelles by branched molecules occurs



at a higher concentration, and accordingly it is possible with such compounds to obtain lower interfacial tensions — down to 0.04 dyn/cm, and by their use it is very easy to produce stable emulsions. When a paraffin oil containing oleic acid is poured into a sodium hydroxide solution spontaneous emulsification takes place, even without stirring. Stackelberg, Kolckner, and Mohrhausen (12) explain this by assuming that the oleic acid molecules are ionised by the alkaline solution and the interface between the oil and water is thereby expanded. Bulges are formed which are cut off and cast off electrically from the interface. Hereby whirl movements arise which cause new bulges. If the oleic acid is not added to the oil phase, but is added in form of soap to the water phase, no spontaneous emulsification occurs.

Whereas it takes a long time for the surface tension of the soap solution to adjust to a constant value, the interfacial tension between a soap solution and an oil phase adjusts itself in a short time. Alexander (29) ascribes the former to a slow penetration and reorientation of the hydrocarbon part of the soap molecules at the air-water interface. At the water-oil interphase, however, the hydrocarbon part freely moves in the oil phase.

*F. Adsorption at the interface.*

Addition of a capillary active compound that lowers the interfacial tension will, in agreement with Gibbs' classical work, lead to an accumulation of the compound at the interface. The adsorption isotherm is a curve with increasing slope which implies that a relatively large quantity of the compound is adsorbed from dilute solutions. Van den Tempel (13) has tried to estimate the potential decrease from drop to liquid from the adsorbed amount of emulsifier as calculated by Gibb's law. He has obtained values of the same order of magnitude as the zeta potential determined from electrophoresis measurements.

Griffin (14) determined the extent of the adsorption experimentally, and tried by measuring the area of the interface to find out how large an area is taken up by a single soap molecule. The work has been extended further by Fischer and Harkins (15). They worked with emulsions consisting of equal parts of paraffin oil and sodium oleate solution produced in a mechanical mixer. The contents of oleic acid and sodium ion were determined in the soap solutions before the experiment, as well as in the aqueous phase from an emulsion which had been stored for such a long time that a separation into layers had taken place. The area of the interface was also determined with an accuracy of 5 % as estimated by the authors by microscopic measurement of a large number (2—3000) of drops. Sodium hydroxyde was added to most of the emulsions in order to suppress the hydro-

lysis. The influence of sodium hydroxide on the particle size was small.

For emulsions produced using an excess of sodium hydroxide determinations of both the oleic acid and the sodium ion contents gave areas per soap molecule from 24 to 38 Å². These are greater than the area 20.5 Å² found for compressed oleic acid films on water. The soap molecules are then not packed as densely in the emulsion as the acid molecules in the monomolecular layer. In emulsions produced from very dilute soap solutions, the area may be as high as 40—50 Å². In such emulsions, some of the drops will fuse on standing and the area per molecule will decrease until it corresponds to a closely packed monomolecular layer. Such emulsions can be stored for years without any increase in the interfacial area. For emulsions where sodium hydroxide has not been added to suppress hydrolysis, sodium analysis gave the areas, of the above mentioned magnitude whereas oleic acid determinations gave areas which were smaller than 20,5 Å² per molecule. The author draws attention to the fact that this should not be interpreted as a formation of a bimolecular layer at the interface, as McBain and Dubois (17) assert, but simply by the fact that oleic acid produsedby hydrolysis dissolves in the oil drops. By repeated shaking of a soap solution with warm toluene, it is possible, as Krafft and Wiglow (16) have shown, to extract the whole content of fatty acid from the soap into the toluene phase. Griffin also is of the opinion that the oleic acid is dissolved in the oil phase.

Martin and Herman (26) have examined emulsions consisting of 60 % petroleum, benzene or nonyl alcohol and 40 % N/30 sodium oleate where no sodium hydroxide had been added to suppress hydrolysis. On the basis of the sodium ion and oleic acid contents in the aqueous liquid phase, the amount of sodium, calculated as sodium oleate, present in the interface was calculated. For the petroleum and benzene emulsions, it was 13.3 and 13.6 % respectively. The amounts of oleic acid which had been removed from the liquid were calculated to be 25.7 and 25.5 % respectively. This corresponds to a degree of hydrolysis of the sodium oleate of 12 %. If this number is compared with the one mentioned earlier for the sodium oleate solution it is seen that the hydrolysis is promoted by the emulsification.

The area per soap molecule in the petroleum emulsion is 29 Å², in good agreement with Fischer and Harkin's measurements. For the benzene emulsion, which was more finely grained, the area was 74 Å², however, The weakly hydrophilic benzene molecules evidently compete with the soap molecules for the positions in the interface. The soap molecules orientate the polar water molecules in the adjoining layers. This hydration increases the stability of the emulsion.



*G. The interfacial viscosity.*

The viscosity of the interface may be estimated by measuring the force necessary to rotate a ring placed in the interface at a certain velocity between two fixed rings concentric with it. The probability for coagulation to take place will be low if the viscosity of the interface is high. Blakey and Lawrence (19) habe not, however, been able to ascertain any interfacial viscosity between sodium oleate solution and toluene. Blakey and Lawrence (20) find similary that the interfacial viscosity is zero for asphalt solutions against a potassium hydroxide solution, whereas it may assume considerable value for asphalt solutions against water.

*H. The stability of elementary emulsified drops.*

Cochbain and McRoberts (21) have measured the lifetime of freshly formed drops of different hydrocarbons in a potassium laurate solution over which layers of the hydrocarbons were poured. The longest lifetime was obtained for a laurate concentration which was a little higher than the CMC. Osipow, Birsan, and Snell (22) obtained similar results in an experiment where the emulsifying medium was a solution of an alkyl sulphonate. At a concentration below the CMC, the lifetime varies as the square root of the ratio of the concentration to the CMC. Similar results were obtained for some dilute emulsions (0.2 % disperse phase). For concentrated emulsions, the optimal stability is obtained with concentrations considerably greater than the CMC (23, 24).

*I. Chemical reactions.*

King and Mukherjee (25) have proposed a method for estimating the stabilities of emulsions. They calculated the interfacial area from the measured diameters of the particles, and found that the interfacial area decreases linearly with time. The reciprocal of the decrease per unit time, $\xi$, is proposed as a measure of stability. For an emulsion consisting of 8 parts of olive oil in 12 parts of 0,01 N sodium oleate, $\xi$ is found to be 44.9. When 0,1, 0,3 and 0,5 part of calcium chloride were added, $\xi$ fell to 16,5, 8,0, and 0, respectively. The effect of the calcium chloride is then an accelerated aging. The addition of 0,1 N hydrochloric acid had a somewhat greater effect than calcium chloride.

Martin and Hermann (26) have examined what happens when different electrolytes are added to a 60 % emulsion of xylene in N/30 sodium oleate. After the addition, some of the emulsion coagulates, and after centrifuging, it is possible to measure the volume of xylene which has separated. The electrolytes were added as decinormal solutions. As an example of the result of the addition of electrolytes, the separated amounts of xylene in

ml after the addition of 0,2 ml of 0,1 N electrolyte are given below.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| HCl | 0.66 | $ZnSO_4$ | 0.23 | $MgSO_4$ | 0.39 | $MgCl_2$ | 0.54 | $Mg(NO_3)_2$ | 0.55 |
| $CaCl_2$ | 0.46 | $SrCl_2$ | 0.49 | $BaCl_2$ | 0.54 | $CuSO_4$ | 0.47 | | |
| $CuCl_2$ | 0.57 | $CoCl_2$ | 0.35 | $Al_2(SO_4)$ | 0.43 | $Th(NO_3)_4$ | 0.55 | | |

That magnesium salts have a large coagulating effect is due to the fact that magnesium oleate stabilized with magnesium hydroxide is an especially effective emulsifier for water in oil.

As mentioned earlier, the hydrolysis of the soap is promoted by the emulsification, and therefore the soaps which are formed on addition of electrolytes will often be acid soaps. The more acidic the metal soaps are, the stronger is the coagulating effect. The authors have analysed the separated metal soaps and found, for example, that the aluminium soap is more acidic than the zinc soap in agreement with the fact that aluminium salts are more effective coagulation agents than zinc salts. With copper, the precipitated copper oleate is taken up by the oil phase. Oleic acid, which is a peptising agent, is hereby removed from the interface. Therefore copper salts are especially effective coagulating agents.

It is interesting to note that the specific chemical reactivities of the individual salts cast doubt upon the earlier mentioned rules relating to the coagulation of lyophobic colloids of oppositely charged ions. Even Schulze and Hardy's rule is no longer valid. Divalent magnesium is as effective as tetravalent thorium.

Sulphates are slight less effective than chlorides and nitrates, as their dissociation is less complete.

Martin and Hermann made the important observation that dilute emulsions are influenced less by small amounts of salts than concentrated emulsions: with dilute emulsions the reaction takes place more in the liquid phase than in the interface.

King and Wrzeszinski (27) have found that when the emulsifier cannot form a water-insoluble salt with multivalent metals, the electrolyte stability will be relatively small. For two such emulsions van den Tempel (28) found that the electrolyte stability follows Schulze and Hardy's rule.

## References


1. *Powney and Wood:* Trans. Faraday Soc. **36,** (1940) 57.
2. *Coehn and Raydt:* Am. Physic **30,** (1909) 777.
3. *Bikermann:* Trans. Faraday Soc. **36,** (1940) 154.
4. *Powis:* Z. physik. Chemie **89,** (1914) 186.
5. *Verwey:* Trans. Faraday Soc. **36,** (1940) 192.
6. *Eilers and Korff:* Trans. Faraday Soc. **36,** (1940) 229.
7. *Derjaguin:* Acta physicochim. **14,** (1941) 633.
8. *Verwey and Overbeck:* Theory of the Stability of Lyophobic Colloids, Amsterdam, 1948.





9. *Ostwald:* Kolloid Z. **85,** (1938) 134.
10. *Cheesman and King:* Trans Faraday Soc. **36,** (1940) 241.
11. *Hartley:* Trans. Faraday Soc. **37,** (1941) 130.
12. *Stalckelberg, Klockner and Mohrhausen:* Kolloid Z. **115,** (1949) 53.
13. *Van den Tempel:* Rec. trav. chim. Pays-bas **72,** (1953) 419.
14. *Griffin:* J. Am. Chem. Soc. **45,** (1923) 1648.
15. *Fischer and Harkins:* J. Phys. Chem. **36,** (1932) 98.
16. *Krafft and Wiglow:* Ber. Deutsch. Chem. Ges. **28,** (1895) 2566.
17. *McBain and Dubois:* J. Am. Chem. Soc. **51,** (1929) 3534.
18. *Martin and Hermann:* Trans. Faraday Soc. **37,** (1941) 25.
19. *Blakey and Lawrence:* Disc. Faraday Soc. **18,** (1954) 268.
20. *Blakey and Lawrence:* J. Inst. Petroleum **40,** (1954) 203.
21. *Cockbain and McRoberts:* J. Colloid Science **8,** (1953) 440.
22. *Osipow, Birsan and Snell:* J. Am. Oil Chem. Soc. **34,** (1957) 34.
23. *Tyuzyo:* Bull. Chem. Soc. Japan, **31,** (1958) 117.
24. *Harkins:* Physical Chemistry of Surface Films. New York, 1952.
25. *King and Mokherjee:* J. Soc. Chem. Ind. **38,** (1939) 243.
26. *Martin and Hermann:* Trans. Faraday Soc. **37,** (1941) 30.
27. *King and Wreszinski:* Trans. Faraday Soc. **35,** (1939) 741.
28. *Van den Tempel:* Rec. trav. chim. Pays-bas, **72,** (1953) 442.
29. *Alexander*: Trans. Faraday Soc. **37,** (1941) 130.

## Finska Kemistsamfundets verksamhet

Protokoll fört vid Finska Kemistsamfundets årsmöte den 10 december 1962 i Tekniska Föreningens i Finland lokal. Förhandlingarna leddes av ordföranden fil.dr. *O. Forsander* med undertecknad *Enari* vid protokollet. Närvarande 19 medlemmar.

§ 1. Ordföranden öppnade mötet och hälsade särskilt kvällens föredragshållare från Åbo välkommen.

§ 2. Förrättades val av styrelse för år 1963. Enligt stadgarna kvarstår i styrelsen fil.dr *Ch. Gustafsson* och fil.dr *O. Forsander*. Till ordförande valdes bitr.prof. *J. Gripenberg* till viceordförande fil.dr *T-M. Enari* och till övriga medlemmar prof. *T. Enkvist*, fil.dr *J. J. Lindberg*, prof. *A. Sundgren* och tekn.dr *J. Sundman*. Till sekreterare för treårsperioden 1963—1965 valdes fil.lic. *N-E. Saris*.

§ 3. Kassören fil.kand. *Karin Sandelin*, arkivarien dipl.ing. *Anna Grönvik* och redaktören fil.dr *T-M. Enari* återvaldes. Till revisorer återvaldes fil.dr *W. Forsman* och tekn.dr *G. Silén* med fil.mag. *B. C. Fogelberg* som suppleant.

§ 4. Skattmästaren framförde budgetförslaget för år 1963, som godkändes. Medlemsavgifterna och funktionärsarvodena bibehölls oförändrade.

§ 5. Mötesdagarna för år 1963 fastslogs. Sålunda samlas Samfundet till ordinarie möte den andra måndagen i februari, mars, april, oktober, november och december.

§ 6. Centralrådet för Finlands Kemister budget för år 1963 godkändes.

§ 7. Ordföranden meddelade att Samfundets styrelse beslutat tilldela docent *R. Gräsbeck* bergsrådet Alfthans pris för år 1962 för hans artikel "Contributions to the Biochemistry and Physiology of Vitamin $B_{12}$ and Intrinsic Factor" som ingått i Meddelandena n:o 3—4, 1961.

§ 8. Fil.lic. *Ebbe Still* från Åbo Akademi höll ett föredrag om "Grafiska metoder för bestämning av ekvivalenspunkter".

§ 9. Efter mötet följde samkväm.

*O. Forsander.* *T-M. Enari*

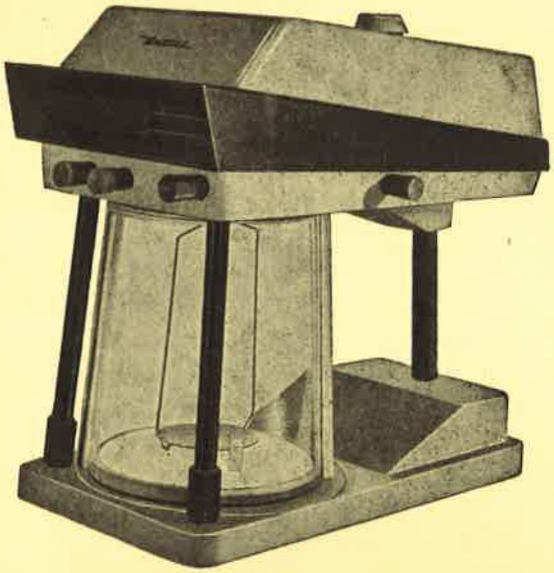
## Litteratur

Karl Rast: *Laborpraxis, Band 4, Chemie für Labor und Betrieb.* Umschau Verlag, Frankfurt a.M. 1960, 124 sidor, DM 7,80.

I serien har tidigare utkommit delarna: 1. Prüfungsbuch für Chemielaboranten, 2. Glasbearbeitung im Labor och 3. Anleitung zur qualitativen Analyse. I den nu föreliggande delen behandlas enkelt men ingående en rad vanliga laboratoriemetoder. I de åtta kapitlen behandlas tvättning av kärl, filtrering, exsikatorer, gastvättflaskor, smältpunktsbestämningsapparater, platinakärl, analysvågar och olycksfallsskydd. Som av listan framgår har alla nyare fysikaliska apparater utelämnats och boken lämpar sig också bäst som en första införing i laboratoriearbeten vid undervisningen.

*T-M. Enari*

# Mettler



## Analysvåg modell S

med digital avläsning

- Större optiskt avläsningsområde
- Vågbalken temperaturkompenserad
- Koncentriska ringvikter
- Differential luftdämpning
- Större vägningsutrymme


**S-5 Makro** Maximibelastning 160 g, avläsning direkt med 5 decimaler, den femte antingen 0 eller 5.


**S-6 Semi-Mikro** Maximibelastning 80 g, avläsning direkt med 6 decimaler, den sista 0 eller 5.

Helsingfors - Fabiansgatan 14
Tel. 11 541

GWB
G. W. BERG & Co

Helsingfors 1963, Frenckellska Tryckeri Aktiebolaget