

## Size determinations of crystallites and hydrophilic/hydrophobic domains in polycrystalline lamellar soaps by x-ray diffraction

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**Abstract.** An experimental approach based on x-ray diffraction is presented for the size determinations of crystallites and of hydrophilic/hydrophobic domains in polycrystalline, lamellar soaps. Literature review indicates that the mean shape of a soap crystallite is definable only along its *c*-axis, while no conclusions can be drawn concerning its shape along the *a* and *b*-axes. Nevertheless, it is shown that it is possible to determine the volume average crystallite dimensions and those of hydrophilic/hydrophobic domains contained in them, from a knowledge of polycrystalline soap's short and long *d*-spacings, line widths at half maximum intensity of 001 and *hk*.0 plane reflections, the densities of hydrocarbon and the water layers, the molecular weight and the total fatty matter content of soap. The methods are illustrated using x-ray diffraction data obtained on commercial stearic, lauric, oleic, elaidic, 12-hydroxystearic and 12-ketostearic soaps of practical interest to soap industry.

**Keywords.** Crystallite size ; x-ray diffraction ; x-ray line broadening ; soap structure.

### 1. Introduction

The soap boilers' neat soap (70% soap and 30% hydration water) exhibits an one-dimensional lamellar structure with distinct hydrophilic (i.e. carboxyl groups, Na<sup>+</sup> ions) and hydrophobic (i.e. alkyl chains) domains separated by an interface (Luzzati and Tardieu 1974) and is of a polycrystalline nature (Klug and Alexander 1974). Beyond about 40% hydration water, soap undergoes transition to structures made up of close-packed cylindrical rods arranged in either a two-dimensional hexagonal lattice or a three-dimensional rhombohedral lattice (Vincent and Skoulios 1966). The size of crystallites and of hydrophilic/hydrophobic domains contained in them, in the lamellar soap phase, is recognised as an important factor affecting many of commercial soaps' properties, e.g. plasticity and processability. However, in spite of soaps' long history in science and technology, no experimental determinations of such size parameters have yet been reported in the literature. The purpose of this paper is to put forward an experimental approach for the size determinations of crystallites and of hydrophilic/hydrophobic domains in lamellar, polycrystalline hydrated (30% water) soaps of practical interest to soap industry

(Nagarkar and Subrahmanyam 1975). X-ray diffraction method was chosen since it can not only be applied to size measurements of crystallites as they exist in solid hydrated soap at room temperature (as illustrated in this paper), but also to study *in situ* size variations during or after processing (e.g. heat, shear, compression, etc.)

## 2. Experimental

### 2.1. Preparation of soap samples

Hydrated soaps with 30% water content were prepared by neutralising appropriate molten fatty acids maintained at 90–95°C with sodium hydroxide. The molten soap mass was allowed to remain on the water bath for about one hour before it was allowed to cool to room temperature. X-ray diffractograms were obtained on these soap samples without any further working or processing. Fatty acids of interest to soap industry were used in this study viz. stearic, lauric, oleic, elaidic, 12-hydroxystearic and 12-ketostearic, and these were procured through commercial sources.

### 2.2. X-ray diffraction patterns

Ni-filtered Cu  $K\alpha_1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) from a Philips stabilised 3 kW x-ray generator with diffractometer and recording accessories was used for the x-ray diffraction patterns. The samples were packed in the standard Philips rectangular powder specimen holder and pressed using a special die with approximately 10 lbs pressure. The holder with sample was inserted in the goniometer set-up in the reflection mode and the scanning rate was set at  $1^\circ/\text{min}$  ( $2\theta$ ). The patterns were recorded in the Bragg angular range ( $9^\circ$ – $40^\circ$ ) with  $0.5^\circ$  divergence and receiving slits. Changes were made in the slit assembly to obtain diffraction data at lower Bragg angles ( $1.5^\circ$ – $9^\circ$ ). The  $d$ -spacings and the half-widths ( $\beta_{1/2}$ ) of selected reflections were measured in the usual manner on the original (diffraction) chart recordings (i.e. without corrections to the observed intensities from air scattering, sample thickness, etc.)

## 3. Bilayer model of soap structure and crystallite shape

From x-ray diffraction data on (solid) sodium soaps of varying degrees of hydration reported in the literature (Vold *et al* 1952 ; Luzzati *et al* 1957, 1958 ; Skoulios and Luzzati 1959, 1961 ; Vincent and Skoulios 1966 ; Skoulios 1967 ; Luzzati 1968 ; Gallot and Skoulios 1966 ; Luzzati and Tardieu 1974) and from data obtained in author's laboratory (an example of which is given in table 1) two common features can be identified, viz.,

(i) A single very intense, sharp line at very low Bragg angle of around  $2^\circ$ , followed by 3 to 8 lines of lower intensities terminating at  $10^\circ$ . These low angle diffraction lines give Bragg  $d$ -spacings in the simple, regular, integral ratios of  $1 : 1/2 : 1/3 : 1/4 : 1/5$ , etc. which are characteristic of one-dimensional lamellar lattice structure (Skoulios and Luzzati 1959). The most intense of these low angle diffraction lines is designated as reflection from the 001 plane. These low angle reflections

Table 1. X-ray diffraction data on commercial Na-stearate (70 TFM).

$2\theta$ (degree)	$\sin \theta$	$d$ (Å)	Intensity (cps)	$d_{001}/d$	Line width $\beta_{1,2}$ (radians)
<i>Long spacings</i>					
2·05	0·0178	43·28	43,088	1·0	0·0043
4·10	0·0358	21·51	1,097	2·0	..
6·10	0·0532	14·48	2,615	3·0	..
8·15	0·0710	10·85	132	4·0	..
10·15	0·0884	8·71	277	5·0	..
<i>Short spacings</i>					
19·55	0·1697	4·54	248	9·5	..
22·35	0·1936	3·98	152	10·9	..
23·00	0·1994	3·86	301	11·2	0·0105
24·90	0·2156	3·57	109	12·2	..

(i.e. long spacings) are usually of the order of the lengths of soap molecules, which are in the range of 18·06 to 25·62 Å for C<sub>12</sub> to C<sub>18</sub> fatty acid anions (Davidsohn *et al* 1953).

(ii) A group of usually 3 to 5 lines of very much lower intensities and somewhat broader (compared to the intense, sharp low angle x-ray diffraction lines) occurring at higher Bragg angles (20 to 40°). These lines give rise to much shorter  $d$ -spacings of the order of the effective widths of soap molecules, which are in the range 3·50 to 5·50 Å (Vold 1952 ; Epstein 1950 ; Davidsohn *et al* 1953). These short  $d$ -spacings do not bear any simple, regular, integral relationships to the most intense 001 plane reflection.

It can be seen that these two main features of x-ray diffraction patterns from a hydrated soap polycrystal (30% water) arise from the transverse and the lateral molecular organisations to be found in soap crystallites, i.e. in the plane perpendicular to the interfacial plane dividing the hydrophilic and the hydrophobic domains and in the plane parallel to the interface, respectively. The idealised bilayer model of soap structure proposed by Luzzati and his co-workers (Luzatti *et al* 1957; Luzatti and Tardieu 1974) and illustrated in figure 1 takes into account only the molecular organisation in the transverse direction and says nothing about organisation in the lateral direction. A somewhat similar view had earlier been expressed by Vold *et al* (1952) who considered soap structure as being composed of (stacked slabs) two-dimensional lamellae and the several feasible molecular conformations in the lateral direction of soap crystallites leads to a multiplicity of as yet poorly defined phase modifications. The mean shape of a soap crystallite is, therefore, structurally definable only in its transverse or the  $c$ -axis, while no conclusions can as yet be drawn concerning the shapes in the other two lateral directions or along the  $a$  and  $b$ -axes; we indicate this uncertainty by the use of circular profile in the drawing shown in figure 1. Similar instances of partially understood crystallite shapes are known to occur *vis-a-vis* crystallites of markedly anisotropic shapes Klug and Alexander 1974) e.g. precipitated Ni(OH)<sub>2</sub>.

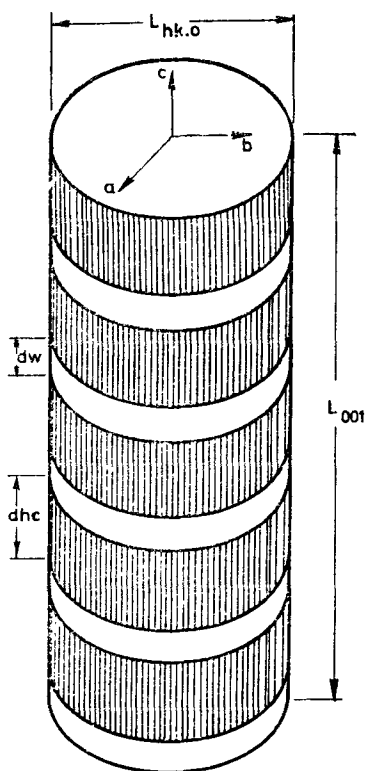


Figure 1. Bilayer model of lamellar soaps.

#### 4. Size determinations of soap crystallites

In the absence of appreciable amounts of lattice imperfections or stacking faults in a sample (Vold *et al* 1952), the crystallite size is given by the well-known Scherrer equation (Scherrer 1918; Klug and Alexander, 1974) as generalised by Stokes and Wilson (1942) viz.,

$$L_{hkl} = \lambda / \beta_{1/2} \cos \theta \quad (1)$$

where,  $L_{hkl}$  is the effective volume average crystallite dimension (in Å units) normal to the reflecting plane  $hkl$ ;  $\lambda$  is the wave-length in Å units which is 1.5406 Å for Cu  $K\alpha_1$ , radiation;  $\beta_{1/2}$  is the line breadth at half the maximum intensity (of the line at  $2\theta$ ) given in radian units.

For mean crystallite size calculations reported here, we have chosen the most intense 001 plane reflection (from the low angle region) and the most intense of the large angle reflections (i.e.  $hk\cdot 0$  reflections) from the large angle region for the measurement of half-widths of lines. Table 2 illustrates the use of equation (1) to crystallite size determinations of hydrated model soaps (all containing about 70 weight per cent soap) carried out in our laboratory.

Table 2. Mean crystallite dimensions of some commercial soaps (70 TFM).

Soap (Na-salts)	Transverse direction to 001 plane				Lateral direction to 001 plane			
	$2\theta$ (degree)	$\cos \theta$	$\beta_{1/2}$ (radians)	$L_{001}$ (Å)	$2\theta$	$\cos \theta$	$\beta_{1/2}$ (radians)	$L_{hk\cdot o}$ (Å)
Stearate	2.05	0.9998	0.0043	359	23.00	0.9799	0.0105	150
Laurate	2.66	0.9997	0.0049	315	22.10	0.9815	0.0131	120
Oleate	2.02	0.9998	0.0061	252	21.55	0.9824	0.0663	23.7
Elaidate	2.04	0.9998	0.0070	220	22.70	0.9804	0.0218	72.1
12-hydroxystearate	1.85	0.9987	0.0038	405	22.40	0.9810	0.0095	158
12-ketostearate	1.75	0.9999	0.0026	593	24.30	0.9776	0.0038	415

### 5. Size determinations of hydrophilic/hydrophobic domains in soap crystallites

Luzzati's bilayer model of soap structure (cf. figure 1) assumes that the carboxyl portion and the  $\text{Na}^+$  ions lie wholly within the aqueous layer, while the alkyl chains are within the hydrocarbon layer. From a knowledge of the soap's long  $d$ -spacing parameter (i.e.  $d_{001}$ ), the density of the hydrocarbon portion, the density of aqueous layer after correcting for the presence of  $-\text{COO}^-$  and  $\text{Na}^+$  moieties, the molecular weight of fatty acid and the total fatty matter (TFM) in the soap specimen, we have calculated the relative thicknesses of the aqueous lamella (i.e.  $d_w$ ) and of the hydrocarbon lamella (i.e.  $d_{hc}$ ). The computation procedure employed is given below:

$d_{hc}$  = Thickness of hydrocarbon lamella (Å);  $d_w$  = Thickness of aqueous lamella (Å);  $d_{001}$  = Long spacing of 001 planes from x-ray evidence;  $b$  = (Arbitrary) equal sides of the simple orthorhombic volume element (Å units);  $\rho_{hc}$  = Density in  $\text{kgm dm}^{-3}$  of hydrocarbon  $C_{(n-1)}H_{2(n-1)+2}$  or  $C_{(n-1)}H_{2(n-1)}$  hydrocarbon for saturated and unsaturated fatty acid anion with  $n$  carbon atoms;  $\rho_w$  = Density in  $\text{kgm dm}^{-3}$  of water containing  $-\text{COONa}$  head group (assumed equal to  $\text{HCOONa}$  of appropriate concentration determined by TFM and molecular weight of fatty acids);  $W_{hc}$  = Weight fraction of hydrocarbon portion in soap (calculated from TFM and molecular weights of fatty acid anion,  $\text{Na}^+$  ion and hydrocarbon portion). The following equalities are obvious from figure 1:

$$\text{weight of hydrocarbon lamella} = d_{hc} \cdot b^2 \cdot \rho_{hc} \quad (2)$$

$$\text{weight of aqueous lamella} = d_w \cdot b^2 \cdot \rho_w \quad (3)$$

$$(d_{hc} + d_w) = d_{001} \quad (4)$$

Dividing (3) by (2):

$$(d_w \cdot b^2 \cdot \rho_w / d_{hc} \cdot b^2 \rho_{hc}) \text{ is also equal to } (1 - W_{hc}) / W_{hc} \quad (5)$$

Rearranging (5) and substituting  $d_{hc} = (d_{001} - d_w)$ ,

$$\text{we get : } d_w = \frac{d_{001} \cdot \rho_{hc} (1 - W_{hc})}{\rho_w W_{hc} + \rho_{hc} (1 - W_{hc})} \quad (6)$$

Table 3. Dimensions of hydrophilic/hydrophobic domains in commercial soaps.

Soap (Na-salts)	$W_{ho}$	$\rho_{ho}$ (kgm dm <sup>-3</sup> )	$\rho_w$ (kgm dm <sup>-3</sup> )	$d_w$ (Å)	$L_{hk,0}^2 \times d_w$ (Å <sup>3</sup> )	$d_{h_0}$ (Å)	$L_{hk,0}^2 \times d_{h_0}$ (Å <sup>3</sup> )
Stearate	0.59	0.77	1.111	14.07	316,500	29.21	657,200
Laurate	0.56	0.75	1.146	11.28	162,800	22.05	317,800
Oleate	0.59	0.80	1.106	14.56	8,177	28.96	25,770
Elaidate	0.59	0.78	1.106	14.24	74,010	29.04	151,000
12-Hydroxy- stearate	0.60	0.85	1.098	16.29	406,700	31.56	787,900
12-Keto- stearate	0.60	0.81	1.099	16.70	2,876,000	33.98	5,851,000

The application of equations (6) and (4) for the calculation of the relative thicknesses of hydrocarbon and water lamellae in soap crystallite, is illustrated in table 3. The densities of hydrocarbons and aqueous Na-formate are taken from standard hand-books (Richter 1941; Weast 1978).

The effective volumes of the hydrophilic and the hydrophobic domains in a soap crystallite are given by  $L_{hk,0}^2 \times d_w$  and  $L_{hk,0}^2 \times d_{h_0}$  respectively, since  $L_{hk,0}$  denotes the volume average crystallite size in one-dimension and its square, the projected cross-sectional area in the lamellar plane. Columns 6 and 8 of table 3 give these dimensions for the six model soaps studied in our laboratory.

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