

## Crystal Structure of Silver Salts of Fatty Acids

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Seven silver salts of even-numbered *n*-fatty acids were investigated by X-rays at 20 and at 78° C. Their unit cells were determined from powder photographs; they proved to be triclinic with two molecules of silver salt per unit cell. At 20° C. the unit cell varies gradually with chain length from  $a=4.588$ ,  $b=4.016$ ,  $c=20.41$  A.,  $\alpha=101^\circ 12'$ ,  $\beta=102^\circ 28'$ ,  $\gamma=80^\circ 4'$  for silver caproate, to  $a=4.693$ ,  $b=4.120$ ,  $c=50.35$  A.,  $\alpha=104^\circ 35'$ ,  $\beta=93^\circ 59'$ ,  $\gamma=76^\circ 1'$  for silver stearate.

Changes of the unit-cell dimensions with temperature have been observed. A packing of the molecules in the unit cell is suggested.

### Introduction

Little is known about the crystallography of silver salts of fatty acids. As we expected that soaps of heavy metals might be easier to study by X-rays than sodium soaps, since the presence of a heavy atom causes lines with high indices to appear stronger, silver soaps were chosen for our study in the hope that they might throw more light on the structure of sodium soaps.

As we expected, the powder lines appeared sharper and the resolution of photographs better than for sodium soaps, and the powder patterns proved to be closely related to  $\xi$  and  $\epsilon$  forms of sodium soaps of Buerger, Smith, Ryer & Spike (1945). These forms were previously suspected by us to be triclinic. As we shall see later, the structure of silver soaps proved to be triclinic, giving valuable evidence in support of the triclinic structure of the above forms of sodium soaps.

The intercomparison of the powder photographs of silver soaps prepared by us shows that they are all in the same form. It should be noted, however, that there exist other forms of silver soaps, as one sample of silver stearate from another source proved to be a mixture of forms different from that studied in this paper.

### Preparation of the specimens

Pure potassium soaps prepared by neutralization of pure fatty acids with alcoholic potash served as starting material. Fatty acids of the highest purity were used.

The lower acids (caprylic to myristic) were obtained by fractional distillation of palm-kernel fatty acids. The lauric and myristic acids were subsequently recrystallized from ethanol. The palmitic and stearic acids were obtained by fractional distillation of the methyl esters of fatty acids of fully hydrogenated palm oil and subsequently twice recrystallized from ethanol.

The constants of the fatty acids used are given in Table 1.

The silver soaps were prepared by adding the calculated amount of aqueous solution of silver nitrate to solutions of potassium soaps in 20% ethanol and 80%

Table 1. *Fatty acids used*

Acid	Mean equivalent molecular weight by titration	Melting-point (° C.)	Setting-point (° C.)
Caprylic	144.1	—	16.4
Capric	172.0	31.8	30.6
Lauric	200.2	44.8	43.9
Myristic	228.3	54.6	53.7
Palmitic	256.4	63.1	62.5
Stearic	284.2	70.3	69.4

water. The silver soaps were precipitated owing to their low solubility in water and separated by filtration. After thorough washing with water and then with ethanol, the precipitates were air-dried at room temperature and kept in darkness. They formed finely crystalline white powders.

### X-ray technique

The powder photographs of the samples were taken in our 12.5 cm. Frevel focusing camera described by Vand (1948*a*). A Metrovick 'Raymax' demountable tube with aluminium windows served as a source of  $\text{Cu } K\alpha$  radiation filtered with nickel foil, the exposures being about  $2\frac{1}{2}$  hr. at 46 kV. and 25 mA. The specimens were mounted between two cellophane sheets, and their thickness was chosen to be equal to the reciprocal value of their linear absorption coefficient.

Photographs of the soaps were also taken at 78° C., and it was observed that certain lines showed a displacement from the position measured on the photographs taken at room temperature. These data were of assistance in indexing the lines of the powder photographs, as lines belonging to the same band had a similar displacement.

### Long spacings and angle of tilt

The study of long spacings is of importance, as it indicates the angle of tilt of the chains with respect to the ionic sheet and throws some light on whether or not all the members of the series are in the same form. The

long spacings of the silver soaps could be expressed within experimental error by the formula

$$1/c^* = A + BN, \quad (1)$$

where  $N$  is the number of carbon atoms in the chain. The constants  $A$  and  $B$  were determined by the Gaussian method of least squares. They are, expressed in Ångström units:

At 20° C.:  $A = 5.291 \pm 0.034$ ,  $B = 2.412 \pm 0.003$ .

At 78° C.:  $A = 5.596 \pm 0.084$ ,  $B = 2.385 \pm 0.007$ .

The agreement between the observed and the calculated values is good, as can be seen from Tables 2 and 3, but the high-temperature measurements are of less accuracy. The observed values of  $c^*$  are weighted means from all the accurately measurable orders, the  $l$ th order usually being taken as having a weight  $l$ .

Table 2. Long spacings of silver soaps at 20° C. in Ångström units

Soap	$c^*$	$1/c^*$ (obs.)	$1/c^*$ (calc.)	Difference obs. - calc.
Silver caproate	0.05056	19.78	19.76	+0.019
Silver caprylate	0.04078	24.52	24.58	-0.064
Silver caprate	0.03396	29.45	29.41	+0.042
Silver laurate	0.02920	34.25	34.23	+0.018
Silver myristate	0.02562	39.03	39.05	-0.025
Silver palmitate	0.02277	43.91	43.88	+0.03
Silver stearate	0.02054	48.68	48.70	-0.02

Table 3. Long spacings of silver soaps at 78° C. in Ångström units

Soap	$c^*$	$1/c^*$ (obs.)	$1/c^*$ (calc.)	Difference obs. - calc.
Silver caproate	0.05030	19.88	19.90	-0.02
Silver caprylate	0.04054	24.67	24.67	0
Silver caprate	0.03391	29.49	29.44	+0.05
Silver laurate	0.02913	34.33	34.21	+0.12
Silver myristate	0.02575	38.84	38.98	-0.14
Silver palmitate	0.02290	43.66	43.75	-0.09
Silver stearate	0.02057	48.62	48.52	+0.10

It is useful to introduce a concept of a *strictly homologous series* of crystals of long-chain compounds, which we shall define as a series of substances differing only in chain length, whose lattice parameters remain strictly constant except those directly dependent on the chain length. Thus, in the strictly homologous series, the dimensions of the ionic sheet, given by the  $a$ ,  $b$  axes and the angle  $\gamma$ , and the plane and tilt of the chains, remain constant, whereas the  $c$  axis and possibly the angles  $\alpha$  and  $\beta$  vary. Real series of substances are only *approximately homologous*, since all the lattice constants vary more or less with the chain length.

The angle of tilt calculated from the increments of the long spacings is quite sensitive to the departures from a strictly homologous series. As MacArthur (1944) has pointed out, its calculation implies not only the constancy of tilt, but also the constancy of the gaps between the chain ends and of the distance between alternate carbon atoms from compound to compound. The values of tilt so calculated must thus be regarded with reserve.

The average distance between alternate carbon atoms is not known with certainty. If tetrahedral bond angles are assumed and the carbon-carbon bond length as found in diamond by Riley (1944) is taken to be 1.5445 Å., the distance between alternate carbon atoms in the chain is 2.5221 Å. In strontium laurate examined by Morley & Vand (1949), this distance has been found to be 2.610 Å., which, in conjunction with the value of 2.598 Å. obtained from potassium caprate by Vand, Lomer & Lang (1947, 1949), gives a more probable mean value of 2.604 Å. On this basis, the angle of tilt for the soaps at 20° C. is 67° 50' and at 78° C. is 66° 18'.

#### Determination of the unit cell

In order to determine the dimensions of the unit cell, a third graphical method of Vand (1948c) of indexing powder photographs of long-spacing compounds was used. The reader should consult this paper and also the previous paper by Vand (1948b) for the symbols used and the theory.

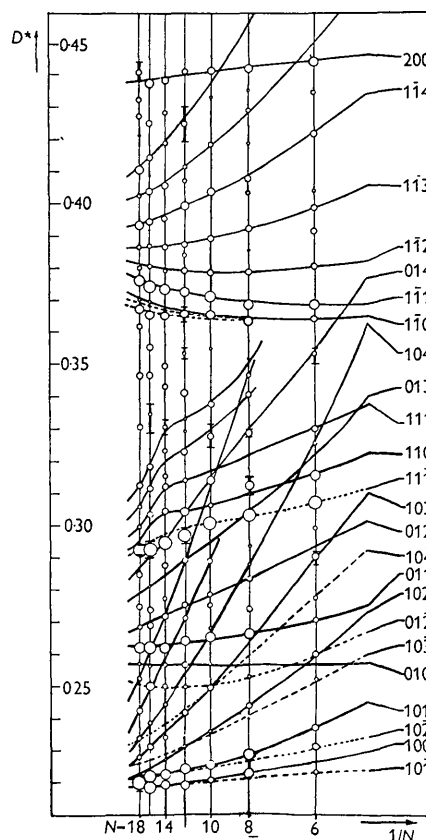


Fig. 1. Reciprocal-spacings diagram for silver soaps at 20° C., showing indexing of the powder patterns. Lines connecting points with negative Miller  $l$  indices are shown broken. Areas of circles are proportional to the observed intensities. The curves are drawn through points calculated from the lattice constants.

It was found advantageous to prepare a graph of  $D^*$  against  $1/N$  for all the lines, where  $D^* = n/d$  are the reciprocal spacings of the powder lines, and  $N$  the

number of carbon atoms in the chain. This graph is shown in Fig. 1 for soaps at 20° C. If the series were strictly homologous, then in this graphical presentation, lines of the same Miller indices throughout the homologous series would approximate to parabolas. However, the variations of the lattice parameters contribute to a distortion of the curves from the parabolic shape. Such effect may be observed particularly in the 111 band.

Using the third graphical method, practically all the powder lines were accounted for by one, two or more sets of Miller indices, the number of superpositions increasing with the Bragg angle. However, the number of lines indexed with certainty was sufficient to evaluate the parameters of the unit cell.

In order to help to co-ordinate the results for soaps of different chain length, it was found of great help to introduce the concept of a *constant direction*. This also gave an independent value of the angle of tilt and served as a guide to the probable packing of the molecules.

Let us consider a strictly homologous series. If  $\alpha_0$  and  $\beta_0$  are the angles of the axis of the chain with the  $b$  and  $a$  axes respectively, they remain the same for the whole series; they do not necessarily coincide with  $\alpha$  and  $\beta$  of the lattice.

From the lattice theory,

$$L^* = lc^* + K^*,$$

where  $K^* = hA^* \cot \beta^* + kB^* \cot \alpha^*$ .

Let  $K_0^* = hA^* \cot \beta_0^* + kB^* \cot \alpha_0^*$ ,

where  $\alpha_0^*$ ,  $\beta_0^*$  are obtained from  $\alpha_0$ ,  $\beta_0$  by the usual reciprocal-space transformations. Then

$$L^* = lc^* + K_0^* + (r + l_0)c^*,$$

where  $0 \leq r < 1$  is constant for a strictly homologous series and  $l_0$  is a whole number. They are defined by

$$(r + l_0)c^* = K^* - K_0^*.$$

It should be noted that  $r=0$ , when the direction of the chain axis coincides with one of the possible  $c$  axes of the lattice.

As  $\frac{1}{2}pc^* = K^* = K_0^* + (r + l_0)c^*$ , we can write  $\frac{1}{2}p - r - l_0 = K_0^*/c^*$ .

If all the possible values of  $p$  are thus plotted against  $1/c^*$ , points lying on a family of parallel straight lines are obtained, the slope of which is  $2K_0^*$  and the intercepts for  $1/c^* = 0$  are  $p = 2r + 2l_0$ .

Even when the series is not strictly homologous, a good approximation to a system of straight lines is obtained, and the angles  $\alpha_0^*$ ,  $\beta_0^*$ ,  $\alpha_0$  and  $\beta_0$  can be evaluated from their slope.

These angles define the *constant direction* of a homologous series, even in a more complicated case where there exist more than one chain direction. In this case the constant direction would be different from the chain directions, and its angle of tilt would be different from the angles of tilt of the chains. The constant direction is

not as sensitive to small departures from a strictly homologous series as the angle of tilt derived from long spacings, so that the theory developed for a strictly homologous series can be applied to real substances.

We employed the constant direction as an additional aid in indexing. The values of  $p_{10}$ ,  $p_{01}$ ,  $p_{11}$  and  $p_{\bar{1}\bar{1}}$  were plotted against  $1/c^*$  and a satisfactory family of straight lines was obtained, thus confirming correctness of our indexing. In Fig. 2 only one line of each family is drawn.

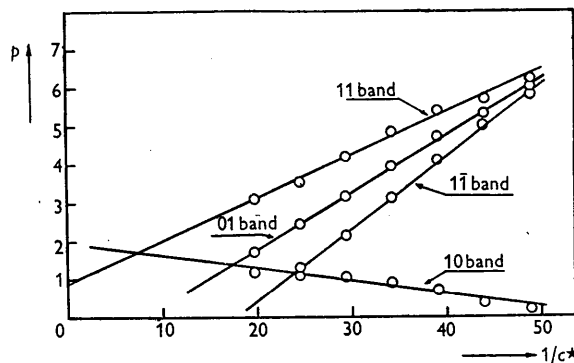


Fig. 2. Plot of  $p$  against long spacing for silver soaps at 20° C. Only one line of each family is drawn.

From these the following values for the constant directions were obtained:

From the 01 band,  $B^* \cot \alpha_0^* = 0.074$ .

Taking average  $B^* = 0.2502$  (value for silver caprate), we have  $\alpha_0^* = 73^\circ 34'$ .

From the 10 band,  $A^* \cot \beta_0^* = -0.02$ .

Taking  $A^* = 0.2193$ , we have  $\beta_0^* = 95^\circ 12'$ .

Therefore the constant direction angles are

$$\alpha_0 = 105^\circ 50' \quad \text{and} \quad \beta_0 = 88^\circ 6'.$$

As in our case the constant direction should coincide with the chain direction, we can calculate the angle of tilt from

$$\sin \tau = \sin \alpha_0^* \sin \beta_0.$$

Thus we obtain  $\tau = 73^\circ 24'$  from the constant direction, whereas  $\tau = 67^\circ 50'$  is obtained from the long spacings.

The relevant constants and the resulting dimensions of the unit cell of silver soaps at 20 and 78° C. are given in Tables 4 and 5. The primary parameters  $A^*$ ,  $B^*$ ,  $c^*$ ,  $\alpha^*$ ,  $\beta^*$  are given, since these are known with greater accuracy than the derived cell constants  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ . The angle  $\gamma$  can be calculated either from  $A^*$ ,  $B^*$  and  $H_{11}^*$  or from  $A^*$ ,  $B^*$ ,  $H_{\bar{1}\bar{1}}^*$ . Both values were calculated in order to check the consistency of the data, but only the mean value is given in the table. The observed densities were determined by flotation, using mixtures of acetone, chloroform, carbon tetrachloride and tetrabromoethane. Silver soaps did not react with these liquids at room temperature, but at 78° C. the densities could not be measured as the soaps decomposed.

The spacings, intensities and probable Miller indices of the powder patterns are not reported here in full, as

they were sent to A. J. C. Wilson for the *X-ray Diffraction Index for the Identification of Materials*;† only one table of spacings for a typical soap, namely, silver caprate at 20° C., is included in Table 6.

### Discussion of the lattice parameters

Tables 4 and 5 indicate that all the soaps studied by us are in the same crystallographic form, the unit cell of

which is triclinic and contains two molecules of silver salt. The space group is thus either  $C_1^1-P1$  or  $C_1^1-P\bar{1}$ . However, the series is not strictly homologous, i.e. the parameters of the unit cell which characterize the form are not strictly constant but vary slightly as a function of the chain length and temperature. This effect can probably be interpreted by the interplay of the ionic forces arising in the ionic sheet and the van der Waals forces between the hydrocarbon chains. Such effects have been already discussed by Vand & de Boer (1947).

† Published by the American Society for Testing Materials.

Table 4. *Silver soaps: parameters of the unit cell at 20° C.*

Soap	Silver caproate	Silver caprylate	Silver caprate	Silver laurate	Silver myristate	Silver palmitate	Silver stearate
A*	0.2213	0.2200	0.2193	0.2198	0.2189	0.2192	0.2196
B*	0.2528	0.2493	0.2502	0.2496	0.2489	0.2486	0.2502
c*	0.05056	0.04078	0.03396	0.02920	0.02562	0.02277	0.02054
$\alpha^*$	80° 16'	78° 42'	77° 53'	77° 1'	76° 32'	76° 23'	76° 1'
$\beta^*$	81° 11'	84° 11'	85° 22'	86° 35'	87° 39'	88° 58'	89° 28'
$\gamma$ (mean)	80° 4'	79° 38'	78° 57'	77° 53'	78° 23'	77° 3'	76° 1'
a (A.)	4.588	4.621	4.646	4.653	4.663	4.682	4.693
b (A.)	4.016	4.078	4.072	4.097	4.102	4.128	4.120
c (A.)	20.41	25.24	30.31	35.33	40.30	45.32	50.35
$\alpha$	101° 12'	102° 23'	103° 9'	103° 51'	104° 9'	104° 13'	104° 35'
$\beta$	102° 28'	97° 48'	96° 57'	95° 59'	95° 3'	94° 7'	93° 59'
$\rho$ obs. (g.cm. <sup>-3</sup> )	2.043	1.838	1.686	1.588	1.506	1.452	1.403
$\rho$ calc. (g.cm. <sup>-3</sup> )	2.062	1.843	1.695	1.597	1.521	1.463	1.423

Table 5. *Silver soaps: parameters of the unit cell at 78° C.*

Soap	Silver caproate	Silver caprylate	Silver caprate	Silver laurate	Silver myristate	Silver palmitate	Silver stearate
A*	0.2200	0.2203	0.2187	0.2189	0.2194	0.2202	0.2182
B*	0.2501	0.2498	0.2469	0.2477	0.2462	0.2462	0.2460
c*	0.05030	0.04054	0.03391	0.02913	0.02575	0.02290	0.02057
$\alpha^*$	80° 26'	79° 8'	77° 31'	77° 26'	76° 35'	76° 2'	75° 55'
$\beta^*$	81° 5'	83° 43'	85° 8'	86° 19'	87° 55'	88° 59'	89° 28'
$\gamma$ (mean)	79° 36'	78° 31'	78° 1'	77° 30'	76° 53'	76° 38'	75° 53'
a (A.)	4.622	4.630	4.674	4.679	4.685	4.668	4.733
b (A.)	4.065	4.085	4.140	4.135	4.176	4.175	4.199
c (A.)	20.48	25.58	30.34	35.30	40.50	45.29	50.21
$\alpha$	101° 12'	102° 13'	103° 17'	103° 35'	106° 38'	106° 30'	104° 38'
$\beta$	100° 47'	98° 27'	97° 24'	96° 22'	94° 6'	93° 57'	94° 2'
$\rho$ calc. (g.cm. <sup>-3</sup> )	2.015	1.822	1.660	1.569	1.509	1.449	1.388

Table 6. *Silver caprate (at 20° C.)*

d/n (A.)	Intensity	Probable index	d/n (A.)	Intensity	Probable index
28.63	1000	001	2.571	20 D	113, 109
14.69	400	002	2.480	30	114
10.02	200	003	2.392	15	115
7.33	50	004	2.309	3	118
5.87	40	005	2.269	30	200, 202
4.91	5	006	2.239	1	201, 203
4.54	20	100, 101	2.217	45	202, 204, 119
4.44	50	101, 102	2.172	20	203, 205, etc.
4.24	10	102, 103	2.121	20	204, 206, 1110
4.01	25	103, 104	2.093	1	1.0.12, 118
3.897	5	010	2.064	1	205, 207, 217
3.772	60	011	1.996	20	206, 208, etc.
3.736	5	104, 105	1.955	20	214, 020, 126
3.638	15	015	1.933	2	207, 209, 127
3.595	15	012	1.887	2	1.1.15, 022
3.461	20	105, 106	1.834	10	1.1.13, 023
3.327	100	111	1.792	10	1.1.16, 024, etc.
3.267	15	110	1.762	7	124, 212
3.187	40	115, 014	1.733	7	2.0.10, 2.0.12, etc.
3.083	20 D	112, 116, 018	1.705	5	218, 125, etc.
3.018			1	126, etc.	
2.965	20	107	1.663	1	127, etc.
2.823	5	019	1.611	1	222, etc.
2.742	50	111, 112, 110	1.581	1	029, etc.
2.699	70	111	1.541	1	
2.645	20	112			

D = diffuse line

The thermal expansion in  $a$ ,  $b$  and  $\gamma$  seems to be approximately independent of  $N$ . If  $a$  and  $b$  are plotted as a function of  $1/N$ , straight lines are obtained, shown in Fig. 3. However, the angle  $\gamma$  plotted against  $1/N$  gives a curved line; when it is plotted against  $N$ , a fairly straight line is obtained in the region covered by measurements; this is shown in Fig. 4.

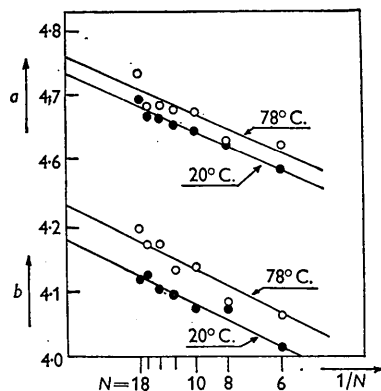


Fig. 3. Dependence of the lattice parameters  $a$  and  $b$  on the chain length and temperature.

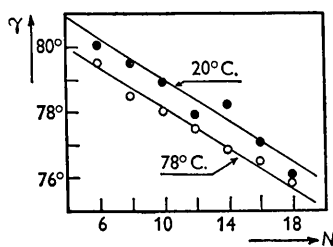


Fig. 4. Dependence of the angle  $\gamma$  on the chain length and temperature.

One can thus write the following empirical relations:

$$a = 4.723 + 0.00047t - 0.88/N,$$

$$b = 4.162 + 0.00090t - 1.00/N,$$

$$\gamma = 1.4399 - 0.00030t - 0.00524N,$$

where  $t$  is the temperature expressed in  $^{\circ}\text{C}$ . and  $\gamma$  is in radians.

In order to investigate the thermal expansion let us take as a representative example  $N = 10$ . Then

$$a = 4.635 + 0.00047t = 4.644 \text{ at } 20^{\circ}\text{C}.,$$

$$b = 4.062 + 0.00090t = 4.080 \text{ at } 20^{\circ}\text{C}.,$$

$$\gamma = 1.3875 - 0.00030t = 1.3815 = 79^{\circ} 08' \text{ at } 20^{\circ}\text{C}.$$

From these equations the ellipse of expansion in the  $a$ ,  $b$  plane was obtained as indicated by Wooster (1938). The equation in rectangular co-ordinates of this ellipse, taking the  $a$  cell edge as  $x$  axis, is

$$x^2(1 - 0.0002t) + y^2(1 - 0.00032t) - xy(0.00064t) = 1.$$

When the axes are rotated through an angle of  $\phi$  equal to  $-38^{\circ} 39'$ , the ellipse becomes

$$\frac{X^2}{(1 - 0.6 \times 10^{-4}t)} + \frac{Y^2}{(1 + 5.8 \times 10^{-4}t)} = 1.$$

The lines of zero expansion are then given by

$$X = \pm 3.109Y.$$

From the above data the thermal expansion diagram was drawn, as shown in Fig. 5.

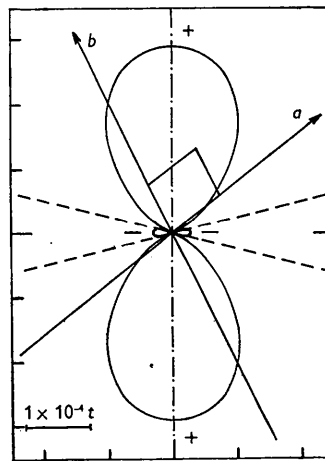


Fig. 5. Thermal expansion diagram. Lines of zero expansion are shown broken.

#### Probable packing of the molecules

A valuable indication of the packing of the molecules can be obtained from the *constant direction* given by  $\alpha_0$  and  $\beta_0$ . These angles enable us to calculate the shortest chain-to-chain distances. One obtains for the distance in a plane comprising the  $a$  axis and the chain axis, 4.65 Å., and in a plane comprising the  $b$  axis and the chain axis, 4.01 Å. Comparing these distances with those found in other long-chain compounds, it is more likely that the planes of the chains are parallel to the  $a$  axis than to the  $b$  axis.

Considering now the ionic sheet, it is probable that this will be a double sheet such as is found in potassium caprate and other soaps. In the top half of the sheet we can place a silver ion at each corner of the two-dimensional lattice. Taking into account the silver and oxygen ionic radii, namely,  $\text{Ag}^+ = 1.13$  Å. and  $\text{O}^{2-} = 1.32$  Å., one arrives at a number of possible packings. However, only the packing shown in Fig. 6 is consistent with the plane of the chains being approximately parallel to the  $a$  axis, *provided* the carboxy group is approximately coplanar with the chain.

The packing of the chains will now be considered. Schoon (1938) demonstrated how several angles of tilt may arise. However, we find his considerations oversimplified. With the aid of Fisher-Hirschfelder-Taylor atomic models, it can be demonstrated that angles of tilt may occur not only in the plane of the chains, but also in other directions. The arrangement with two molecules per unit cell, one at each side of ionic sheet, is the simplest, as all adjacent chains have the same orientation. In other systems, further complications may arise due to possibilities of adjacent chains having different orientation of their axes or planes, or both.

As the silver soaps belong to the simple arrangement with all the axes and planes parallel, all the possible angles of tilt may easily be calculated, provided the distances between adjacent chains are known.

Taking the distance between alternate carbon atoms within a chain 2.604 Å. and the chain-to-chain distance in the plane of the chains 4.65 Å., we obtain the following possible angles of tilt: 90°, 60° 43', 41° 46', etc. None of these angles agrees with the angle of tilt found in silver soaps. However, if the angles of tilt perpendicular to the plane of the chain are considered, the distance between chains being taken 4.01 Å. in that direction, one obtains 72° 03', 45° 45', etc.

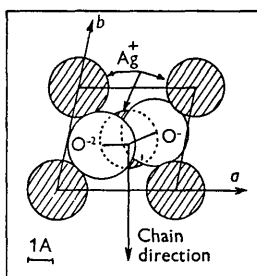


Fig. 6. Probable packing in the ionic sheet. Silver ions at the corners belong to the top half of the sheet and are approximately at the same level as the oxygen ion. The silver ion at the centre belongs to the bottom half of the sheet. The projection of the chain direction on the plane of the sheet is also shown.

The first of the calculated angles taken greater than 90° gives 107° 57', which agrees reasonably well with the component  $\alpha_0 = 105^\circ 50'$  of the constant direction. Accepting this mode of packing, the component  $\beta_0$  will be 90°, which also agrees reasonably well with the observed 88° 6'.

There exist further angles of tilt obtained by considering general directions; however, none agrees with the observed angles. We can thus conclude that in silver soaps, the planes of the chains are approximately parallel to the  $a$  axis and the axes of the chains are tilted in a plane perpendicular to the  $a$  axis; the calculated angles  $\alpha_0 = 107^\circ 57'$  and  $\beta_0 = 90^\circ$  are in good agreement with the constant direction and with the angle of tilt obtained from the long spacings.

We notice that there is a close similarity between the unit cells of silver soaps and the triclinic form of the hydrocarbons, represented by  $C_{18}H_{38}$ , described by

Müller & Lonsdale (1948). The cell dimensions of this hydrocarbon are:  $a = 4.285$ ,  $b = 4.820$ ,  $c = 23.070$  Å.,  $\alpha = 91^\circ 6'$ ,  $\beta = 92^\circ 4'$ ,  $\gamma = 107^\circ 18'$ ; the shorter and longer diagonals in the  $a, b$  plane are 5.413 and 7.339 Å. Silver soaps have similar dimensions in the  $a, b$  plane; especially their shorter diagonal, which varies but little with chain length and temperature, and is nearly identical with that of paraffin. At 20° C. it varies in our series between 5.591 and 5.444 Å., whereas the longer diagonal expands greatly with chain length from 6.597 to 6.953 Å. As the paraffin lattice contracts with increasing chain length, as shown by Vand & de Boer (1947), the trend is such that the triclinic paraffins and the silver soaps would tend to converge to identical dimensions in the  $a, b$  plane for infinite chain length.

The angles of tilt are again similar. There is only one molecule along the  $c$  axis of the paraffins, and their long-spacing increment of 1.216 Å. compares within experimental error with 1.206 Å., which is half the increment for silver soaps.

It is thus highly probable that the triclinic hydrocarbons have the same type of side packing as silver soaps.

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