Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Liquid-Crystalline Structures of Binary Systems α-ω Soap/Water

Bernard R. Gallot [a]
[a] Centre de Biophysique Moléculaire, 45-Orleans-02, France

Version of record first published: 28 Mar 2007.

To cite this article: Bernard R. Gallot (1971): Liquid-Crystalline Structures of Binary Systems α-ω Soap/Water, Molecular Crystals and Liquid Crystals, 13:4, 323-336

To link to this article: http://dx.doi.org/10.1080/15421407108083549

Molecular Crystals and Liquid Crystals. 1971. Vol. 13, pp. 323–336

Printed in Great Britain

Liquid-Crystalline Structures of Binary Systems α-ω Soap/Water†

BERNARD R. GALLOT

Centre de Biophysique Moléculaire
45-Orleans-02
France

Received October 12, 1970

Abstract—We have studied by X-ray diffraction method the structure of binary systems α-ω alkali soap/water. We have shown that these systems exhibit only one liquid crystalline phase of smectic type. We have studied the influence on the structural parameters of the following factors: concentration, temperature, nature of the metal, length of the paraffinic chain, electric state of the polar groups.

Introduction

For several years we have studied, by X-ray diffraction, the structures occurring in anhydrous mono and di alkali soaps as a function of temperature. We have shown that the number of structures possible for disoaps is by far smaller than for monosoaps; if three types of structural elements (lamellae, discs and ribbons) have been identified for monosoaps,[1–6] only one type (lamellae) has been found with disoaps.[7]

Do dialkalisoap-water systems exhibit a similar simplification in their behaviour? In order to answer this question, we have undertaken, by X-ray diffraction, the study of water solutions of potassium and rubidium α-ω soaps with 16 and 22 carbon atoms (α-ω diacids with 16 and 22 carbon atoms being the only diacids commercially available).

We shall indicate these disoaps by: 1–16 K, 1–22 K, 1–16 Rb and 1–22 Rb; the chemical formula corresponding to the 1–22 K soap, for instance, being:

$$KOOC—(CH_2)_{20}—COOK$$

† Presented at the Third International Liquid Crystal Conference in Berlin August 24–28, 1970.

Experimental

Disoaps were prepared by exact neutralization of diacid in methanolic solution by potassium or rubidium methanolate, followed by precipitation and washing with anhydrous ether.

Samples of binary systems were prepared by direct weighing of soap and water. After homogenizing by prolonged heating and cooling to room temperature the mixtures were put into solvent-tight cells in order to examine them with X-rays. The concentration c (grams of soap per gram of solution) of each solution was determined by drying the sample after the X-ray diffraction experiment.

X-ray diffraction measurements were performed in a Guinier type focusing camera, operating in vacuum and equipped with both a bent-quartz monochromator and a device for recording the diagrams of samples heated at high temperatures (kept constant to $\pm 1\,^{\circ}C$).

Results

(A) Description of the Structures

All X-ray diffraction patterns from the liquid crystalline phases can be indexed as follows:

—in the small angle region: a series of three (00l) reflections, typical of a layered structure.

—in the wide angle region: a diffuse halo at 4.5 Å showing that the paraffinic c chains take up a disordered conformation, more similar to that of a liquid paraffin than to that of a crystal.

Therefore, the structure is lamellar and consists of a set of plane, parallel, equidistant sheets; each sheet results from the superposition of two layers: one formed by the hydrophobic paraffinic chains, the other by water; polar groups form an interface between water and hydrocarbon chains in liquid state.

The inter-sheet spacing d is given by X-ray experiments.

The paraffinic layer thickness d_1, the water layer thickness d_2 and the specific surface of the polar groups S are calculated by formulae based on simple geometry:

$$d_1 = \frac{d}{1 + \rho_1/\rho_2 \; 1 - c/c}$$

$$d_2 = d - d_1$$

$$S = \frac{M}{A \rho_1 d_1}$$

where c is the concentration in soap of molecular weight M

ρ_1 the density of soap[8]

ρ_2 the density of water.

(B) Domain of Stability of the Lamellar Structure

The detailed determination of the domains of stability of the liquid-crystalline phases we met with was not the aim of our work. However, we did take care to locate their approximate boundaries, with the sole purpose of being sure to have only one phase in the samples we examined.

Examination of the diffraction diagrams showing supplementary lines in their central part and sharp lines situated in the region of large Bragg angles allowed us to detect phase separation between coagel and lamellar liquid crystalline structure.

Phase separation between lamellar liquid crystalline structure and micellar solution was generally revealed only after calculating the structural parameters, the curves representing them as functions of the composition showing singular points.

(C) Influence of the Concentration

We have plotted the variation of the structural parameters (Tables 1 and 2) of the lamellar structure *versus* soap concentration, in Fig. 1 for the system 1–22 K/water at 121 °C, in Fig. 2 for the system 1–16 K/water at 104 °C, in Fig. 3 for the system 1–16 Rb/water at 86 °C and in Fig. 4 for the system 1–22 Rb/water at 86 °C.

When the soap concentration of the four systems increases:

—the inter-sheet spacing d decreases,

—the soap layer thickness d_1 increases,

—the water layer thickness d_2 decreases,

—the specific surface S decreases.

TABLE 1 Variation of Structural Parameters *Versus* Soap Concentration

Soap	C	d(Å)	d_1(Å)	d_2(Å)	S(Å²)	N
1–22 K (T = 104 °C) ρ_1 = 1,14	$0{,}50_4$	$32{,}5_4$	$14{,}9_6$	$17{,}5_8$	$43{,}5_0$	$4{,}3_5$
	$0{,}52_0$	$32{,}3_2$	$15{,}3_8$	$16{,}9_4$	$42{,}3_2$	$4{,}6_3$
	$0{,}53_9$	$32{,}2_2$	$15{,}9_6$	$16{,}2_6$	$40{,}7_8$	$5{,}0_1$
	$0{,}56_6$	$31{,}9_6$	$16{,}6_8$	$15{,}2_8$	$39{,}0_2$	$5{,}5_7$
	$0{,}59_0$	$31{,}9_2$	$17{,}4_5$	$14{,}4_7$	$37{,}3_2$	$6{,}1_5$
	$0{,}59_8$	$31{,}6_7$	$17{,}5_8$	$14{,}0_9$	$37{,}0_1$	$6{,}3_7$
1–22 K (T = 121 °C) ρ_1 = 1,12	$0{,}50_4$	$32{,}1_5$	$14{,}8_2$	$17{,}3_3$	$44{,}7_0$	$4{,}2_9$
	$0{,}56_6$	$31{,}1_5$	$16{,}3_0$	$14{,}8_5$	$40{,}6_5$	$5{,}5_0$
	$0{,}59_0$	$30{,}9_1$	$16{,}9_3$	$13{,}9_8$	$39{,}1_3$	$6{,}0_7$
	$0{,}64_5$	$30{,}7_2$	$18{,}5_8$	$12{,}1_4$	$35{,}6_7$	$7{,}6_7$
	$0{,}65_8$	$30{,}5_8$	$18{,}9_1$	$11{,}6_7$	$35{,}0_5$	$8{,}1_2$
	$0{,}63_7$	$30{,}4_4$	$19{,}3_0$	$11{,}1_4$	$34{,}3_3$	$8{,}6_8$
1–16 K (T = 104 °C) ρ_1 = 1,24	$0{,}53_8$	$24{,}1_6$	$11{,}4_0$	$12{,}7_6$	$42{,}4_4$	$6{,}1_4$
	$0{,}55_5$	$23{,}8_9$	$11{,}6_9$	$12{,}2_0$	$41{,}4_0$	$6{,}5_7$
	$0{,}57_0$	$23{,}8_1$	$12{,}0_1$	$11{,}8_0$	$40{,}3_0$	$6{,}9_9$
	$0{,}57_9$	$23{,}7_0$	$12{,}1_7$	$11{,}5_3$	$39{,}7_6$	$7{,}2_5$
	$0{,}62_6$	$23{,}3_9$	$13{,}1_5$	$10{,}2_4$	$36{,}8_0$	$8{,}8_2$
	$0{,}64_6$	$23{,}2_3$	$13{,}5_6$	$9{,}6_7$	$35{,}6_9$	$9{,}6_8$
	$0{,}68_5$	$23{,}1_5$	$14{,}4_8$	$8{,}6_7$	$33{,}4_3$	$11{,}4_6$

TABLE 2 Variation of Structural Parameters *Versus* Soap Concentration

Soap	C	d(Å)	d_1(Å)	d_2(Å)	S(Å²)	N
1–22 Rb (T = 86 °C) ρ_1 = 1,23	$0{,}46_0$	$33{,}9_9$	$13{,}6_5$	$20{,}3_4$	$48{,}8_0$	$3{,}3_5$
	$0{,}48_8$	$33{,}3_7$	$14{,}2_3$	$19{,}1_4$	$46{,}8_0$	$3{,}7_1$
	$0{,}51_4$	$32{,}7_9$	$14{,}8_9$	$17{,}9_0$	$44{,}7_3$	$4{,}1_5$
	$0{,}54_6$	$31{,}9_5$	$15{,}5_2$	$16{,}4_3$	$42{,}9_0$	$4{,}7_1$
	$0{,}59_9$	$31{,}1_0$	$16{,}5_2$	$14{,}5_8$	$40{,}3_2$	$5{,}6_5$
	$0{,}61_4$	$30{,}5_5$	$16{,}9_7$	$13{,}5_8$	$39{,}2_4$	$6{,}2_3$
	$0{,}64_2$	$30{,}2_4$	$17{,}7_1$	$12{,}5_3$	$37{,}6_0$	$7{,}0_5$
1–16 Rb (T = 86 °C) ρ_1 = 1,37	$0{,}55_4$	$24{,}2_4$	$11{,}3_3$	$12{,}9_1$	$43{,}7_5$	$5{,}8_8$
	$0{,}60_0$	$23{,}8_7$	$12{,}2_8$	$11{,}5_9$	$40{,}3_7$	$7{,}1_0$
	$0{,}62_5$	$23{,}7_0$	$12{,}8_3$	$10{,}8_7$	$38{,}6_6$	$7{,}8_9$
	$0{,}64_3$	$23{,}5_8$	$13{,}2_2$	$10{,}3_6$	$37{,}5_2$	$8{,}5_4$
	$0{,}66_0$	$23{,}4_0$	$13{,}5_3$	$9{,}8_7$	$36{,}6_5$	$9{,}1_9$
	$0{,}69_5$	$23{,}0_9$	$14{,}2_4$	$8{,}8_5$	$34{,}8_1$	$10{,}7_8$
	$0{,}73_9$	$23{,}2_0$	$15{,}4_6$	$7{,}7_4$	$32{,}0_7$	$13{,}3_8$

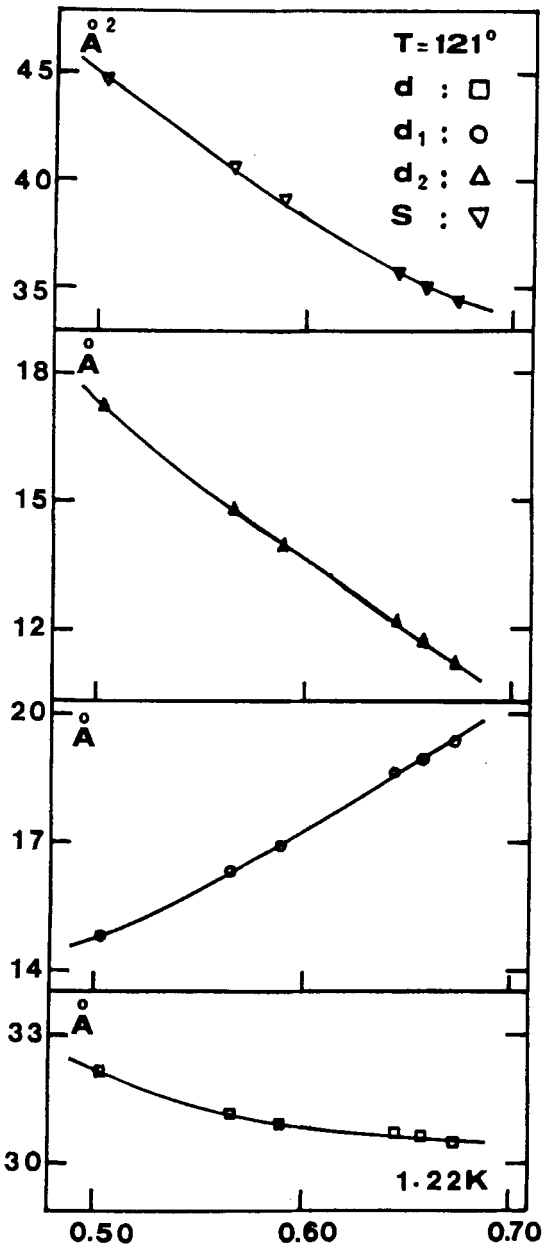

Figure 1.

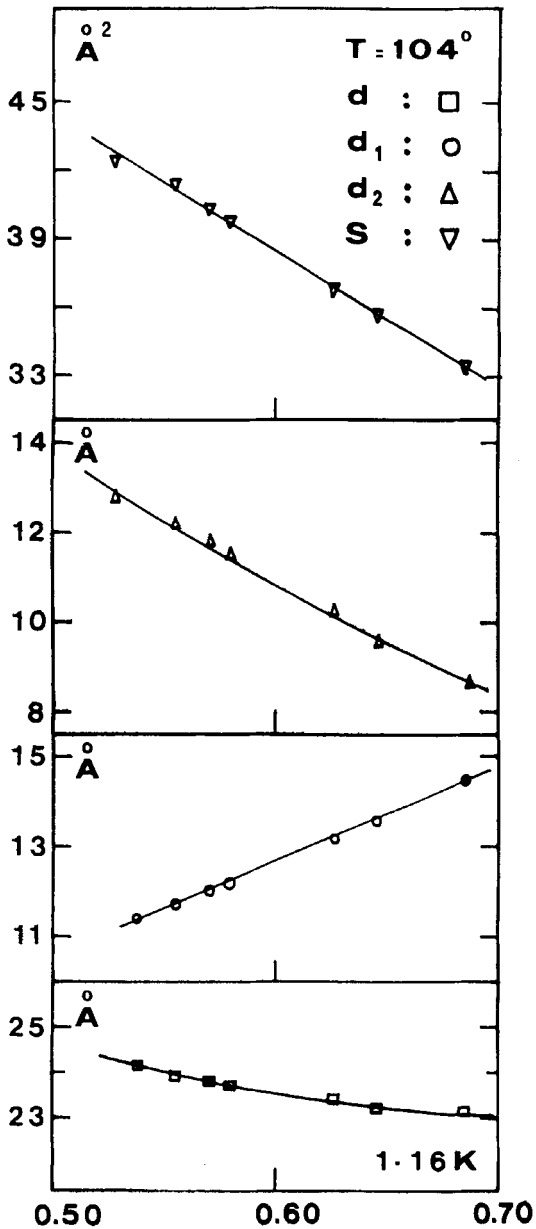

Figure 2.

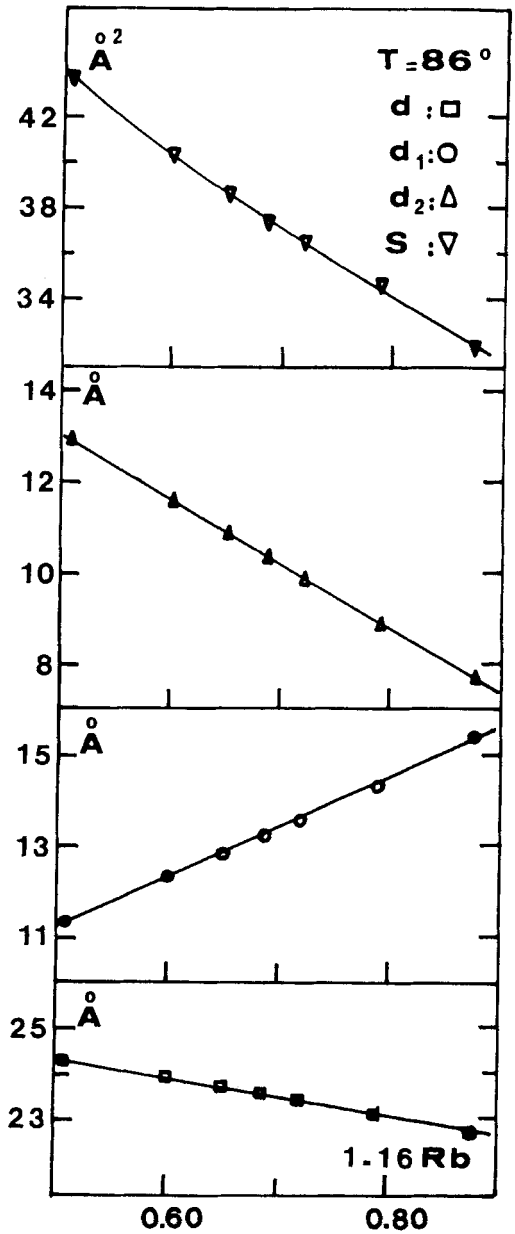

Figure 3.

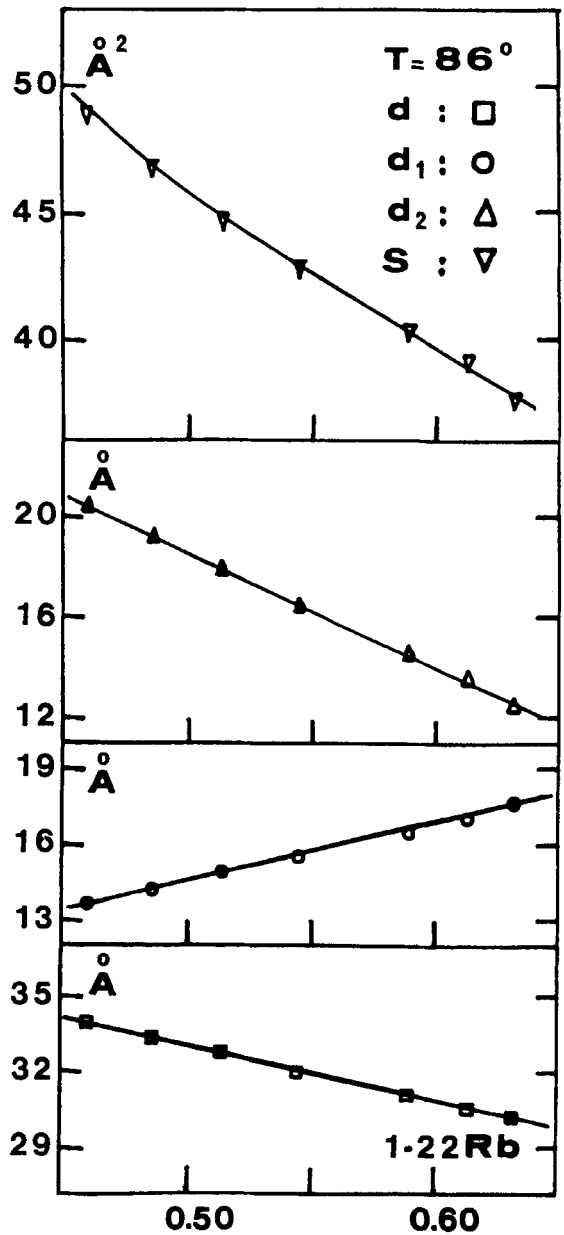

Figure 4.

(D) Influence of the Temperature

In Fig. 5, we have plotted, at constant soap concentration (57%) the variation of the inter-sheet spacing of the three following soaps: 1–22 Rb, 1–22 K and 1–16 K, versus temperature.

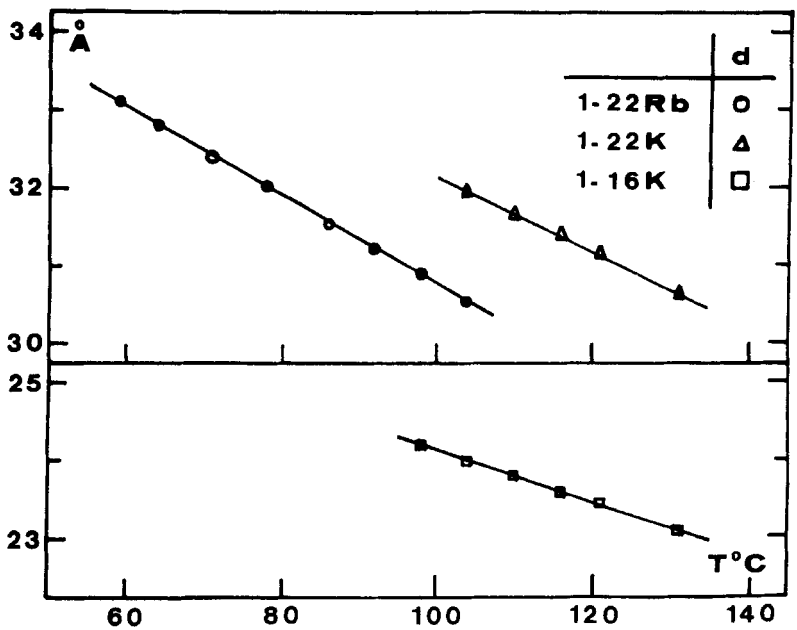

Figure 5.

For the three soaps the inter-sheet spacing d decreases when the temperature increases like in the case of the neat phase of anhydrous soaps.

The values of the linear contraction coefficient $\alpha = 1/d\ \Delta d/\Delta T$ are collected in Table 3.

Table 3 Values of the Linear Contraction Coefficient

Soap	$10^4\ \alpha$
1–22 Rb	17,4
1–22 K	15,4
1–16 K	13,7

(E) Discussion

How can we explain the variation of the structural parameters with concentration, temperature, nature of the polar group, length of the paraffinic chain? What is the respective influence of the electrical state of the aqueous regions and of the configurational energy of the paraffinic chains?

Among the structural parameters we have described, the specific surface is the most interesting to solve this problem, because it immediately reflects the antagonism between polar groups and paraffinic chains. For an identical state of hydration, one can compare soaps of different molecular weight and impute all S variation to the exclusive influence of the configurational energy of the paraffinic chains.

Therefore, to discuss our results, we shall consider the variation of S *versus* N (number of gram molecular weight of soap per litre of water):

$$N = \frac{2000\rho_2}{M} \cdot \frac{c}{1-c}$$

(1) *Case of monosoaps*

In Fig. 6,[9] we have plotted, in a logarithmic representation, the variation of S versus N, at 86 °C, for eight potassium monosoaps from 8 to 22 carbon atoms. All the points representing the variation of S *versus* N fall on the same curve. Therefore S is independent of the length of the paraffinic chain and this conclusion is true for all temperatures as it is shown by Fig. 7.[9]

For monosoaps the variation of S with N is of the type:

$$S = S_0 N^{-p}$$

and it seems that the role of the " electrical state "[9] of the aqueous regions is by far more important than the role of the configurational energy of the paraffinic chains.

(2) *Case of disoaps*

Now let us see what happens with disoaps.

We have plotted the variation of S *versus* N: in Fig. 8 for dipotassium soaps with 22 and 16 carbon atoms and for potassium

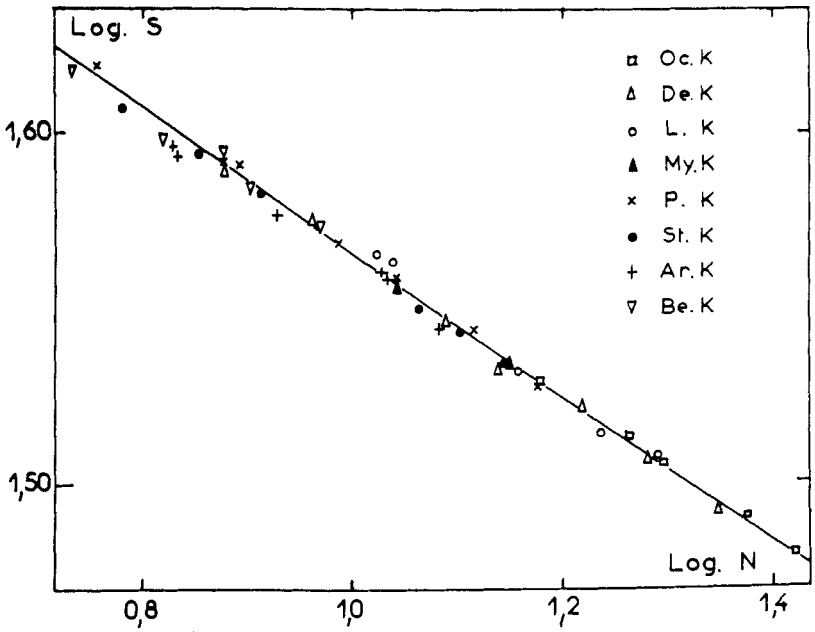

Figure 6.

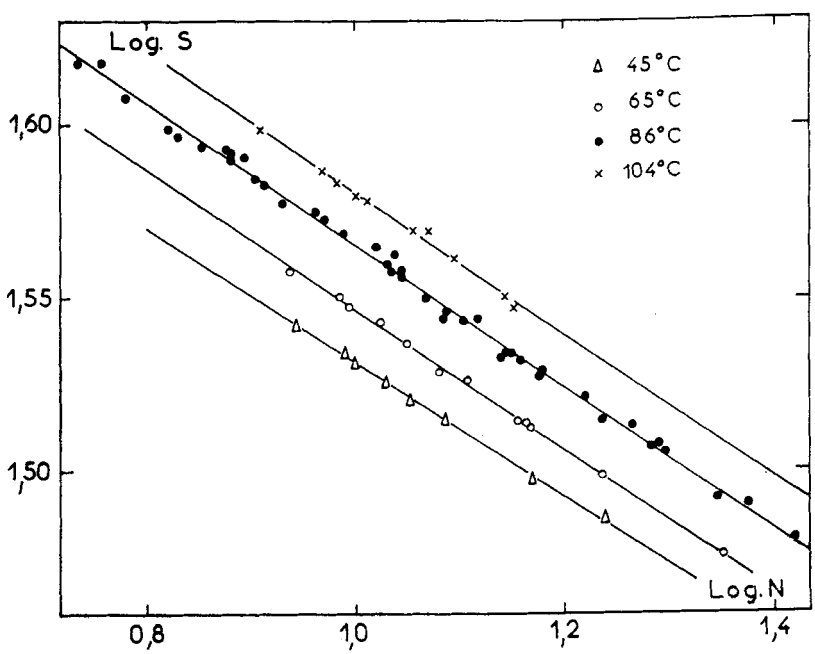

Figure 7.

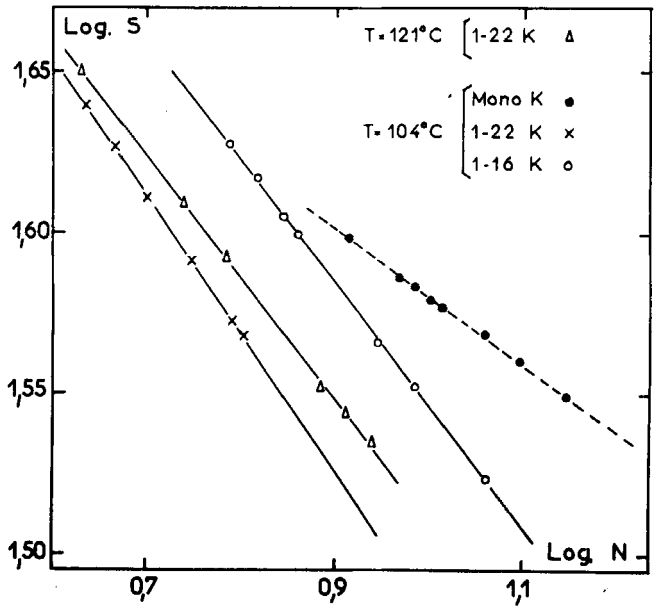

Figure 8.

monosoaps at the same temperature (104 °C) and in Fig. 9 for rubidium disoaps with 22 and 16 carbon atoms and for rubidium monosoaps at 86 °C.

For rubidium soaps as well as for potassium soaps, each disoap has its own curve and the two curves are different from the curve of monosoaps.

Therefore it seems that for disoaps both the " electrical state " of the aqueous regions and the configurational energy of paraffinic chains play a large part.

Conclusion

From the present study, we can deduce two fundamental results concerning binary water-soap systems.

First, if the monosoap-water systems generally exhibit two mesomorphic structures[9,10]: a cylindrical and a lamellar ones, and sometimes three mesomorphic structures (the third being cubic); the α-ω disoap-water systems always exhibit only one mesophase with a lamellar structure.

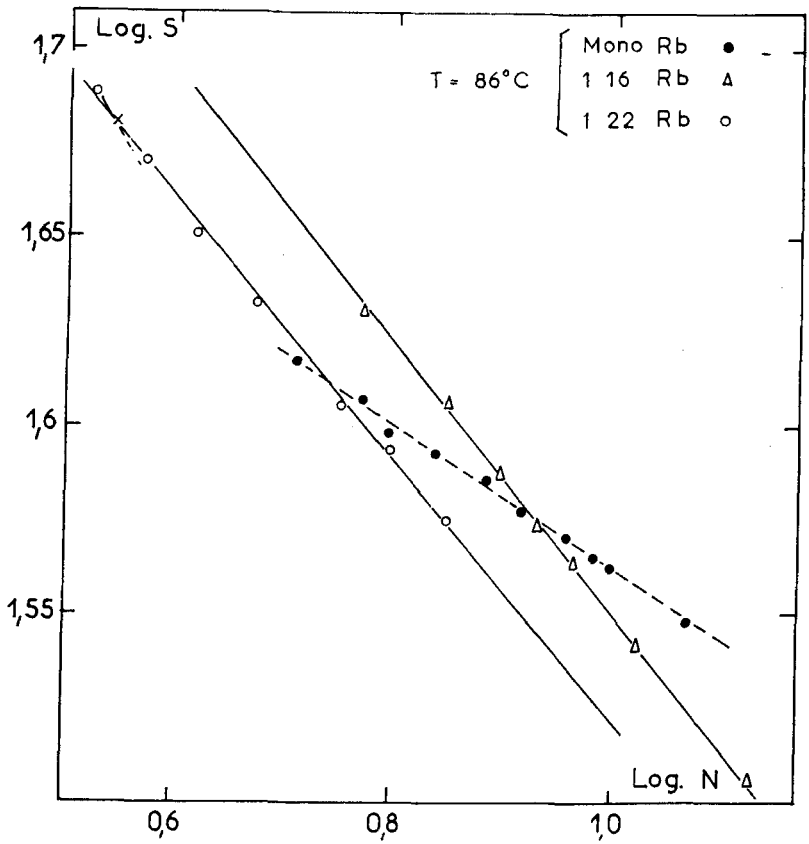

Figure 9.

We may point out a second fundamental difference between water-monosoap and water-disoap systems. In water-monosoap systems, the role of the " electrical state " of the aqueous regions seems by far more important than the role of the configurational energy of the paraffinic chains; while, in water-disoap systems, both the " electrical state " of the aqueous regions and the configurational energy of the paraffinic chains play a large part.

The different behaviour of the two kinds of soaps seems to be the result of the presence of a polar group at each end of the molecule of disoap: this presence reducing the number of configurations allowed to be taken by the paraffinic chain.

Acknowledgements

Discussions with Dr. A. Skoulios are gratefully acknowledged.

REFERENCES

1. Skoulios, A. and Luzzati, V., *Acta. Cryst.* **14**, 278 (1961).
2. Gallot, B. and Skoulios, A., *Acta. Cryst.* **15**, 826 (1962).
3. Gallot, B. and Skoulios, A., *Mol. Cryst.* **1**, 263 (1966).
4. Gallot, B. and Skoulios, A., *Kolloid-Z.u.Z. Polymere* **209**, 164 (1966).
5. Gallot, B. and Skoulios, A., *Kolloid-Z.u.Z. Polymere* **210**, 143 (1966).
6. Gallot, B. and Skoulios, A., *Kolloid-Z.u.Z. Polymere* **213**, 143 (1966).
7. Gallot, B. and Skoulios, A., *Kolloid-Z.u.Z. Polymere* **222**, 51 (1968).
8. Gallot, B., Thèse, Université de Strasbourg (1965).
9. Gallot, B. and Skoulios, A., *Kolloid-Z.u.Z. Polymere* **208**, 37 (1966).
10. Husson, F., Mustacchi, H., and Luzzati, V., *Acta. Cryst.* **13**, 668 (1960).