Some Isotropic Mesophases in Systems Containing Amphiphilic Compounds

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The occurrence of 8 optically isotropic mesophases in binary and ternary systems of amphiphilic compounds and water is reported and the mesophases have been subjected to X-ray diffraction examination. The indexing of the X-ray patterns disclosed the existence of several cubic structures. The nature of them is discussed with account taken of other experimental results such as the volume fraction of the components and the bonding of water to the hydrophilic groups. The extremely stiff mesophases lay in quite different concentration parts of the systems.

Among the mesophases "normal" as well as "reversed" and "complex" structures would seem to be represented. In the system in which both normal and reversed structures were found they lay on each side of a mesophase region with a lamellar structure, the normal on the side with greater amount of water; the complex structures occur on both sides of this region.

As the indexing of the reflections presented difficulties and in some cases was rather unreliable it must be kept in mind that the structure models are tentative and further examination with other experimental methods is required.

Isotropic mesomorphous phases in binary systems of water and fatty acid soaps and of water and a soap-like amphiphilic substance have been described by Luzzati and co-workers,[1-6] Clunie, Corkill and Goodman,[7] Lutton,[8] and Larsson;[9] the first of these authors have observed an isotropic mesophase also in a ternary system of soap, water, and a hydrocarbon.[4] We have previously reported the occurrence of isotropic phases in a number of ternary systems.[10-14] The present article reports the results of a study of the structure in 8 such mesophases. The interpretation is based on the results of X-ray diffraction examinations, combined with data obtained by other methods.

X-Ray diffraction studies performed by the Debye-Scherrer technique showed in all the studied mesophases the presence of a diffuse interference ring, whose position corresponded to a Bragg spacing of about 4.5 Å. It is evident from this that the hydrocarbon parts of the phases are in a semi-
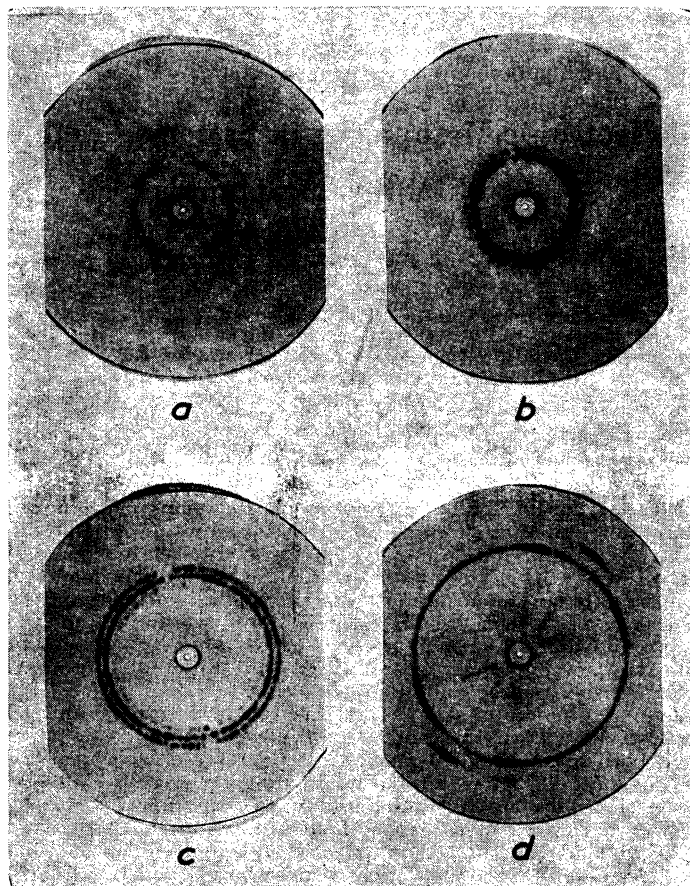
Fig. 1. Typical low-angle X-ray diffraction patterns from isotropic mesophases. Debye-Scherrer technique; Specimen to film distance, 500 mm, $CuK\alpha$-radiation nickelfiltered, scale 1:2.22.

    a. Lauryl decaethylene glycol ether—water system (43:57).
    b. Lauryl decaethylene glycol ether—oleic acid—water system (42.1:36.5:21.4).
    c. Sodium caprylate—p-xylene—water system (40:4:56).
    d. Potassium caprylate—decanol—water system (66:0:34).

liquid state. In addition, close to the primary beam there were from 2 to 7 interference rings. They were granular in appearance, although the specimens were rotated (Figs. 1 a—d). The granular nature of the rings suggests that the secondary structural units in the mesophase must be quite large. Since we are dealing with optical isotropic mesophases they must possess a cubic structure. The indexing of the reflections presented difficulties and for some of the phases it is rather unreliable; it was performed by using $\sin^2\theta$ ratios.

In the interpretation of the inner structure of such mesophases with cubic symmetry it has usually been assumed that the amphiphilic substance is present as spherical particles in a water environment, the hydrophilic groups of the amphiphilic molecules being located in the surface of the spheres.[2,3] In some cases the possibility of a reversed structure has been considered;[6] here spheres of water lie in a continuum of amphiphile, and the hydrophilic groups are oriented inwards towards the water. The X-ray diffraction data alone provide no direct indication of the type of structure of these structural units but only give the distances between the lattice points and suggest that the substance must be in some way symmetrically arranged around them. However, by combining these data with density measurements that give the partial specific volumes of the various components and their volume fractions in the mesophase, it has been possible to calculate the diameter of the assumed spherical particles and the area per hydrophilic group in the boundary surface towards the water, and to compare these values with known molecular dimensions and other data.

It would seem that account must be taken of the fact that all the isotropic mesophases have a particularly stiff consistency, and hence that the mobility of the particles composing the mesophase is inhibited. If the particles are spheres the stiffness of the phases would rule out a structure with liquid, unbound water between the spheres, at least where these approach closest to each other. It would seem that the volume fraction of particle-forming substance must suffice at least to give spheres that touch each other or for the spheres to be deformed to symmetric polyhedrons.

The result of our earlier studies of mesophases show that at least part of the contained water is engaged by, or bound to, the hydrophilic groups of the molecules of amphiphile.[10–12,14,16,17] Some water molecules are subject to ion dipole forces and oriented around the counter ions of the association colloids, and some are bound directly to the hydrophilic groups *via* hydrogen bonds. Up to a certain water content all the water can be bound in this manner, so that it belongs to the substance composing the particles; above this level part of the water in the mesophase will be free. Through this binding of the water the volume fraction of the substance composing the particles is increased, and account of this must be taken in the discussion of the structure of the mesophase.

We have accordingly attempted to ascertain the most probable structural models for the isotropic mesophases in question, and on the basis of these models the dimensions of the particles have been calculated.

THE SYSTEM LAURYL DECAETHYLENE GLYCOL ETHER – OLEIC ACID – WATER

In this system optically isotropic mesophases were observed in two quite distinct concentration regions, I_1 and I_2 in Fig. 2.[10–12] They are separated by quite wide zones containing homogeneous middle soap (region E) and homogeneous neat soap (region D) and by two- and three-phase zones. The isotropic mesophase in I_1 is in equilibrium with the micellar aqueous solution in region L_1 and with the middle soap in region E, while the isotropic mesophase in I_2
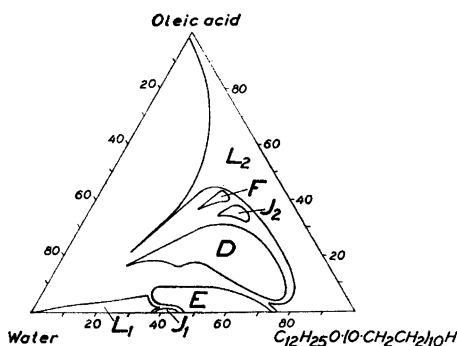
Fig. 2. Triangular diagram showing the location of some of the regions with homogeneous phases in the ternary system lauryl decaethylene glycol — oleic acid — water.

Regions I_1 and I_2 with isotropic mesophases. Region E mesophase with middle soap structure. Region D mesophase with neat soap structure. Region F mesophase with "reversed" hexagonal structure. Regions L_1 and L_2 with isotropic micellar solutions.

is in equilibrium with the reversed two-dimensional hexagonal mesophase in region F, the micellar oleic acid solution in region L_2 and with neat soap in region D. Both the isotropic mesophases are absolutely clear and quite stiff gel-like phases.

In the binary lauryl decaethylene glycol ether — water system the former isotropic mesophase appears at amphiphile contents of 40—44 %; without undergoing any structural change this can incorporate up to 2 % of oleic acid (region I_1).

The X-ray diffraction pattern showed 3 interference reflections in the low-angle region; Table 1 gives the associated Bragg spacings. (The first sample is from region I_1, the second from region I_2).The ratio between the Bragg spacings is: 1:0.706:0.357, which is close to that corre-

Table 1. Isotropic mesophases in the system lauryl decaethylene glycol ether — oleic acid — water.

Composition %			Bragg spacing Å	Intensity	hkl if primitive cubic lattice	if body-centred cubic lattice
Lauryl decaethylene glycol ether	Oleic acid	Water				
42	—	58	54.5±1.5	strong	100	110
			38.5	weak	110	200
			31.5	medium	111	211
					$a_0=54.4$	$=77$ Å
					if face-centred cubic lattice	
42.1	36.5	21.4	54.1±1.5	strong	111	
			46.7	medium	200	
			33.1	very weak	220	
			28.5	weak	311	
					$a_0=94$ Å	

sponding to a primitive or a body-centred cubic unit cell (Table 1). In the case of the primitive cubic packing with 6 closest neighbours the volume fraction of the substance composing the spheres would be 0.52 against 0.68 for the body-centred lattice with 8 closest neighbours. The mere fact that the latter packing is more dense indicates that it is the more probable.

If the specific volume of the mesophase and the components is arbitrarily put at unity the volume fraction of the amphiphilic substance would be between 0.40 and 0.44, so that it does not suffice to form touching spheres in a cubic packing. Viscosity measurements of aqueous solutions of lauryl decaethylene glycol ether have shown that the micellar substance in the concentrated solutions that are in equilibrium with the mesophase in I_1 binds about 21 moles of water per mole of decaethylene glycol ether.[20] In these solutions the volume fraction of hydrated substance forming the micelles is 0.61. It would seem justified to assume that about the same amount of water is bound to the hydrophilic groups of the amphiphiles in the mesomorphous phase; the volume fraction of hydrated substance composing the spheres will then be between 0.64 and 0.71. The fairly close agreement with the theoretical value for a body-centred cubic packing suggests that this indexing of the reflections is correct. The diameter of these spheres of hydrated amphiphilic substance will then be 67 Å: the spheres consist of about 90 molecules of lauryl decaethylene glycol ether and about 2000 of water; the area per molecule in the interface between the amphiphile sphere and the water layer is then 105 Å^2.

The isotropic mesophase denoted I_2 contains about the same amount of lauryl decaethylene glycol ether as that in region I_1 — that is, about 42 % — and, in addition, about 37 % of oleic acid and 21 % of water. The 4 X-ray diffraction spacings are in the ratio 1:0.864:0.612:0.527 which is in quite close agreement with that for spheres in face-centred cubic close-packing. Here, then, is the densest packing of spheres, with 12 closest neighbours, for which the volume fraction of sphere-forming substance is 0.74. The experimentally observed volume fraction of the two amphiphilic components combined lies between 0.79 and 0.84; this does not absolutely rule out a structure built up of spheres composed solely of amphiphile in a water environment, but for various reasons the reversed structure is considered to be the more probable; that is to say, spheres of hydrated amphiphilic substance in which the molecules are oriented with the hydrophilic groups facing inwards and the hydrocarbon chains outwards thus constituting spherical particles with a core consisting of the hydrophilic groups and the water surrounded by a layer of paraffin chains.

Region L_2, with its micellar solution in oleic acid, sends out a narrov salient towards the water corner of the system; this suggests that the solution contains aggregates of lauryl decaethylene glycol ether and oleic acid with a particularly high stability.[11] Infra-red measurements indicate the formation in the solution of a molecular compound with a molar ratio of 1:1 between the components.[20] This compound might also constitute the structural unit of the amphiphilic aggregates in mesophase I_2. This would imply that the lauryl decaethylene glycol ether and about one half of the oleic acid of the mesophase is included in the sphere-forming substance; the particle also contains the water (between 15 and 20 moles per mole of lauryl decaethylene glycol ether),

presumably bound to the hydrophilic groups. This hydrated sphere-forming substance accounts for 0.81—0.83 of the volume. This means so dense a packing of the spherical particles that their outer layer of paraffin chains will be slightly deformed. The radius of the spheres will be about 43.8 Å and that of their core of ethylene oxide groups and water, 29 Å. The area per amphiphilic molecule in the interface between the water-containing core and the surrounding layer of paraffin hydrocarbon chains will be about 60 Å². The oleic acid not included in the sphere occupies the hollows in the lattice.

THE SYSTEM POTASSIUM CAPRYLATE—DECANOL—WATER

In this system a stiff, clear, and optically isotropic mesophase occurs at a ratio of 57—66 parts of caprylate to 0—9 parts of decanol to 34 parts of water (Fig. 3).[18] The quite small region I of homogeneous mesophase extends from the soap-water axis upwards between the large region E of hexagonal middle soap and region D of lamellar neat soap; the isotropic mesophase is in equilibrium with both of these and, *via* a three-phase area, also with solid, crystalline potassium caprylate.

In the low-angle region of the X-ray diffraction pattern for the mesophase there are two granular interference rings (Table 2). The Bragg spacing ratio is 1:0.86, which is close to that for a face-centred cubic unit-cell. On raising the decanol content the unit-cell parameter was found to increase from about 42 to 48.5 Å. Touching spheres would have a diameter between 29.5 and 35.3 Å, and as the volume fraction of the amphiphile (caprylate and decanol) only amounts to 0.64 the spheres must also contain water. Our study of mesophases in systems of potassium soaps have shown that at 20°C no mesophase contains less water than 2.5—3.5 moles per mole of soap; the amount required for the hydration of the potassium ions.[16] In the mesophase of interest in the present connection the water content is constant at about 5.2 moles per mole of amphiphile and 5.2—6.0 moles per mole of caprylate. In order that the

Table 2. Isotropic mesophase in the system potassium caprylate—decanol—water.

| Composition %			Bragg spacing Å	Intensity	hkl if face-centred cubic lattice	a_0 Å
KC$_8$	Decanol	Water				
57.0	9.0	34.0	28.1	strong	111	48.5
			24.2	medium	200	
61.0	5.0	34.0	26.6	strong	111	46
			22.8	medium	200	
63.0	3.0	34.0	25.8	strong	111	44.5
			22.2	medium	200	
66.0	—	34.0	24.8	strong	111	43
			21.3	medium	200	
64.5	—	35.5	24.8	strong	111	43
			21.3	medium	200	

volume fraction of hydrated amphiphile shall exceed 0.74 a minimum of only 2.5 moles of bound water per mole of caprylate would be required. It would seem likely, however, that the rest of the water, too, is bound to the hydrophilic groups (*via* hydrogen bonds to the carboxylate and hydroxyl groups). If this is the case, the particles can no longer be spherical but are dodecahedrons in face-centred cubic packing; each dodecahedron will then be surrounded by a sheath of bound water molecules about 3.5 Å thick. The cross-section of the amphiphile particles would range from 20 to 27 Å and the area per hydrophilic group at its interface would be between 58 and 70 Å².

This model requires that some of the hydrophilic groups of the amphiphile molecules project slightly more than others but this is understandable if there is a radial array and a tight packing of the molecules. A prerequisite for this structure, instead of that of spheres with a smooth surface and all the hydrophilic groups at about the same distance from the centre, is that the whole water content of the mesophase should be bound to the hydrophilic groups; the structure can then be expected only at fairly low water contents; in this case this mesophase structure exist only at a water content close to 5.2 moles per mole of amphiphile.

It is of interest in this context to note that in binary systems of water and a higher potassium soap at 100°C (potassium laurate, myristate, and palmitate) Luzzati and co-workers found an isotropic mesophase with face-centred cubic unit-cell in the area between middle and neat soaps.[2,3] This structure was initially interpreted as spheres of amphiphile in a water continuum. It was, however, later considered that the reversed structure was more likely — that is water spheres in an amphiphile continuum.[6] Support for this opinion was found in the fact that this model gave an area value per hydrophilic group that lay between those computed for neighbouring parts of the regions of the neat and middle soaps. In the opposite alternative the area value was much greater and furthermore the fairly large diameter of the spheres arrived at seemed to be incompatible with the dimensions of the molecules.

The structure of these mesophases at 100°C is with all probability the same as that of the mesophase in the potassium caprylate system at 20°C described by us. The water content of these mesophases rises slightly with chain length — from about 8 to 10 moles per mole of soap — but in all the systems it is, however, so low that all the water could be considered to exist in bound form.

Calculations on the basis of Luzzati's experimental results show that in those cases, too, the model proposed by us leads to an acceptable result. In addition, the objection that a normal structure would be incompatible with the known molecular dimensions is invalid as regards the dodecahedron model. The fact that with this model the area per hydrophilic group is larger than that for the middle soap in the adjacent part of its phase region does not constitute in our opinion a serious objection to the model. It is true that the area per hydrophilic group usually increases on passing from one mesophase with a lower to a neighbouring mesophase with a higher water content, but examples of the opposite trend have also been encountered. In the transition from the lamellar mesophase of region D to the two-dimensional tetragonal mesophase of region C with a higher water content the area increases quite considerably
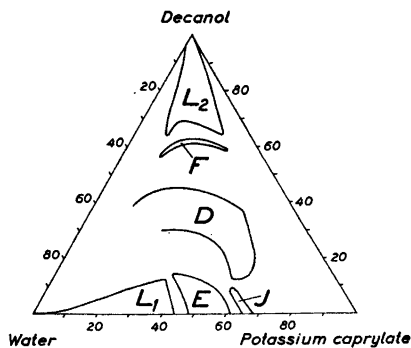
Fig. 3. Triangular diagram showing the location of some of the regions with homogeneous mesophases in the ternary system potassium caprylate — decanol — water.

Region I with isotropic mesophase.
Region E mesophase with middle soap structure.
Region F mesophase with "reversed" hexagonal structure.
Region D mesophase with neat soap structure.
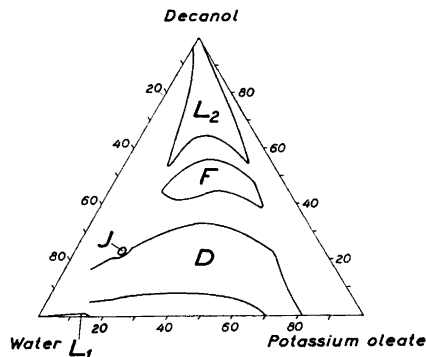
Fig. 4. Triangular diagram showing the location of some of the regions with homogeneous phases in the ternary system potassium oleate — decanol — water.

Region I with isotropic mesophase.
Region E mesophase with middle soap structure.
Region F mesophase with "reversed" hexagonal structure.
Region D mesophase with neat soap structure.

(the area value increases also if the mesophase is considered as a lamellar structure), but on passing further to the lamellar mesophase of region B that has still more water there is a return to lower values (sodium caprylate—decanol—water and potassium caprylate—decanol—water and other similar ternary systems).[15,18,19] Another objection to the reversed structure proposed by Luzzati is the difficulty of explaining why the addition of water to lamellar neat soap produces a change to the "reversed" particle structure instead of to the "normal" structure. On adding more water we have the change to the "normal" hexagonal middle soap structure. The former transformation to the reversed structure would seem to be so remarkable that irrefutable proof must be adduced before it can be accepted.

THE SYSTEM POTASSIUM OLEATE—DECANOL—WATER

In the potassium oleate—decanol—water system, too, there is a stiff clear isotropic mesophase at 20°C, now with the approximative soap—decanol—water ratio of 15:23:62. Its area of existence (I in Fig. 4) is quite restricted, it lying between the large region D of lamellar mesophase and region F with reversed two-dimensional hexagonal mesophase, with both of which this isotropic phase is in equilibrium. As this mesophase is extremely sensitive to temperature it was difficult to obtain satisfactory X-ray photograms. In the low-angle region, however, 4 interference rings were obtained (Table 3) the

Table 3. Isotropic mesophase in the system potassium oleate—decanol—water.

Composition %			Bragg spacing Å	Intensity	hkl if face-centred cubic lattice
$KC_{18:1}$	Decanol	Water			
15	23	62	87	strong	111
			75.2	medium	200
			45.7	weak	311
			38.8	weak	400
					$a_0 = 150$ Å

Bragg spacing ratio of which is 1:0.81:0.53:0.45, which is consistent with a face-centred cubic unit-cell; the reflections with indicees 220 and 222 are absent, however. If the above interpretation is correct the unit cell parameter would be 150 Å, and the diameter of touching spheres 106 Å. The volume fraction of the amphiphile in the phase is about 0.41; to give touching spheres the substance composing spheres must therefore consist of both amphiphile and water. A further 7.7 or so moles of water per mole of amphiphile is required to raise the volume fraction of the hydrated substance to 0.74 — that is about the water content of the aggregates of phase F in that part of the region in equilibrium with the isotropic mesophase.

The idea of a structure of spheres of amphiphile in a water continuum or of water spheres in an amphiphilic environment leads to improbable dimensions. More consistent is a structure of spheres in water continuum and consisting of a double layer of amphiphile around a water nucleus with the same diameter as the core of the rod-shaped aggregates in the left part of the mesophase region F. The molecules of the double layer thus are oriented with their hydrated hydrophilic groups inwards and outwards. The diameter of the water nucleus will then be about 42 Å, the thickness of the amphiphilic layer about 23 Å, and the area per hydrophilic group at the interfaces with the water about 30 $Å^2$.

According to this model the thickness of the layer of amphiphile molecules is slightly smaller than in the adjoining part of the lamellar mesophase D in equilibrium with it. The area per hydrophilic group is about the same as in this part of mesophase D and in the left part of region F.[16]

SYSTEMS CONTAINING HYDROCARBONS

When a hydrocarbon such as *p*-xylene or octane is added to a system of sodium caprylate and water a clear, stiff, optically isotropic mesophase is formed (Figs. 5 a and b, region I).[10,12,13] In both the xylene and the octane systems the region for this phase is quite small and is located at about 40 % of caprylate, 55 % of water and 2—7 % of the hydrocarbon. The mesophases in question are in equilibrium with the micellar aqueous solution in region L_1 and the hexagonal mesophase in E, and with the pure hydrocarbon.
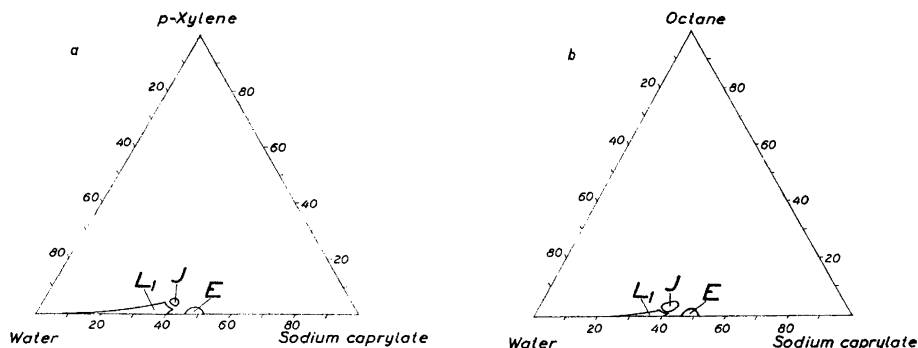
Fig. 5. Triangular diagrams showing the location of some of the regions with homogeneous
phases in the ternary systems:

a. Sodium caprylate—*p*-xylene—water;
b. Sodium caprylate—octane—water.
Region I with isotropic mesophase.
Region E   mesophase with middle soap structure.
» L_1 with isotropic aqueous micellar solution.

The X-ray diffraction data for these mesophases are given in Table 4. The
Bragg spacings as such are not indicative of any of the cubic patterns; only if
it is assumed that the three innermost reflections are extinguished do they
fit a cubic lattice.

For the mesophase containing xylene up to 7 interference reflections were
obtained, for which the ratio d/a_0 is then 0.502:0:445:0.400:0.357:0.319:0.237:

Table 4. Isotropic mesophases in systems of sodium caprylate—hydrocarbon—water.

Composition %			Bragg spacing Å	Intensity	*hkl* if primitive cubic lattice	if body-centred cubic lattice
NaC$_8$	*p*-Xylene	Water				
40	4	56	35.9 ±1.5	medium	200	220
			31.8	strong	210	310
			28.6	strong	211	222
			25.5	strong	220	400
			22.8	weak	310	420
			16.9	weak	411, 330	600, 442
			15.3	weak	332	622
					$a_0 = 72$ Å	$= 101$ Å
	Octane					
40	4.5	55.5	37.3 ±1.5	medium	200	220
			32.7	medium	210	310
			29.9	medium	211	222
					$a_0 = 73$ Å	$= 103$ Å

0.214; this would indicate either a primitive or a body-centred cubic packing. If the indexing is correct the unit cell dimension will be about 101 Å.

In the xylene system the volume fraction of the amphiphilic and lipophilic substances together will be 0.42—0.45. This value is obtained on the basis of specific volumes of 1.16 cm^3/g for xylene, 0.908 cm^3/g for sodium caprylate, and 0.968 cm^3/g for water, (the last 2 are experimental values for region E of the system). The value for the volume fraction is even lower than that for spheres in the least dense cubic packing. It is thus evident that in the case of spheres of amphiphile the spheres in this mesophase are composed of hydrated substance in a water environment (the most logical arrangement for a mesophase in equilibrium with an aqueous micellar solution). The water content of the phase, about 13 moles per mole of caprylate, is higher than for the hexagonal phase E, and also higher than the greatest amount that can be bound directly to the hydrophilic groups of the soap; hence, not all the water can belong to the sphere-forming substance.

Moreover, it is known that no mesophases in the sodium caprylate system has a lower water content than 5—6 moles per mole of caprylate. If, as a first assumption, the above minimum amount of water is included in the substance composing the spheres the volume fraction of hydrated caprylate and xylene will be 0.69—0.70; this is consistent with a body-centred cubic packing of spheres provided that they are slightly deformed.

Touching spheres in a unit cell of the above mentioned dimension (101 Å) will have a diameter of about 88 Å. Unless we abandon the assumption that all the hydrophilic groups of the amphiphilic molecules lie in the amphiphile/water interface, spheres with this diameter cannot exist (already the unhydrated sphere will have a diameter of about 80 Å and the length of the caprylate molecule is about 12 Å). The spheres must have a complex structure. One possibility is that they are composed of double layers of amphiphile molecules around a water nucleus. The hydrocarbon chains of each layer are facing each other and the hydrated hydrophilic groups are facing outwards. Another possible structure is an innermost sphere of amphiphile with the hydrated hydrophilic groups facing outwards, this sphere in turn surrounded by a concentric double layer of hydrated molecules with hydrocarbon chains within the layer.

In the present case the former structure is inconsistent with the assumptions, while the latter is more compatible with the derived dimensions. The body-centred packing requires that 32 % of the water will fill the empty spaces between the complex spheres. The diameter of the nuclear sphere, less the thickness of the hydration shell, will then be about 33 Å; the surrounding water will be about 6 Å and the double layer of amphiphile molecules about 17 Å thick. Outermost these complex spheres are surrounded by an about 4 Å thick layer of bound water molecules. The area per hydrophilic group in the amphiphile/water interface has been estimated to about 47 Å^2 per molecule.

Similar conditions exist in the isotropic mesophase containing octane. Three X-ray reflections were observed (Table 4), and applying the same interpretation as in the previous case we obtain for the ratio d/a_0 (where a_0 is 73 or 103 Å) the values 0.512:0.448:0.410. Here, too, the volume fraction of hydrated caprylate and octane will be 0.69—0.70 and the unit-cell dimension

in the body-centred cubic lattice, 103 Å. The diameter of a simple sphere will then be 89 Å. Thus, if the assumptions are correct, we have here, too, spheres with a complex structure. The most plausible solution is then the same complex structure as in the case of xylene.

Only a calculation of the fluctuations in intensity of the various reflections on the basis of the derived complex structure can establish the correctness of the assumption that the three innermost reflections are extinguished, and show whether the structure arrived at is the correct one. In this connection, however, it may be noted that for a hexagonal mesophase of a binary system where the innermost reflection was much weaker than the others, Luzzati and co-workers found agreement between the experimentally observed intensities for the reflections and the derived values for an assumed complex structure.[3]

Of interest in this connection is the isotropic mesophase that the Luzzati group observed in the sodium myristate—ethyl benzene—water system (at about 29 % of myristate, 50—60 % of water and 11—12 % of hydrocarbon).[4] This has been assigned a face-centred cubic structure with a unit-cell dimension of about 130 Å; this would give unhydrated simple spheres of amphiphile with a diameter of about 80 Å in a water environment. Here, too, if this model is correct, the spheres must obviously have a hydration shell, and the sphere-forming substance would be accompanied by about 8.5 moles of water per mole of myristate. The difference from the caprylate—hydrocarbon cases may be due to the fact that myristate hydrocarbon chain is almost twice as long and that here the water content per mole of soap in the isotropic phase is much higher.

SYSTEMS CONTAINING CHLORINATED HYDROCARBONS

When the hydrocarbon in the ternary systems concerned in this study is replaced by a chlorinated hydrocarbon such as chlorooctane or tetrachloromethane a clear, stiff optically isotropic mesophase is obtained in roughly the same concentration region as for the hydrocarbon containing systems [20] (Figs. 6 a and b; region I). In the chlorooctane system the approximate proportions are: caprylate about 40, water about 50, chlorooctane 5—10. In the tetrachloromethane system the ratio is about 35:56:5—8. The X-ray diffraction patterns are similar to those obtained for the hydrocarbon systems with 3 to 5 granular rings. The associated Bragg spacings are given in Table 5. The chlorine atoms appear not to affect the relative intensity of the various reflections. The indexing and interpretation of the structure are the same. The unit-cell dimensions of the body-centred cubic lattice are about 109 and 102 Å, respectively. The diameters of touching spheres will be 94 or 88 Å. Complex spheres of the same structure as in the hydrocarbon cases will then have nuclei with the diameters 40 or 34 Å, surrounded in turn by a water layer about 6 Å and an amphiphilic double layer 20 or 17 Å thick. Outermost the complex spere is surrounded by a 4 Å thick layer of bound water. The area per hydrophilic group in the amphiphile/water interfaces is about 42 or 44 Å^2.
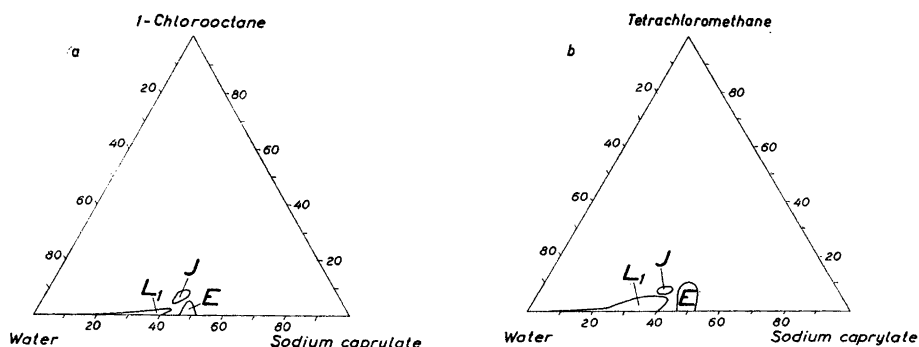
Fig. 6. Triangular diagram showing the location of some of the regions with homogeneous phases in the ternary systems:

a. Sodium caprylate — chlorooctane — water;
b. Sodium caprylate — tetrachloromethane — water.
Region I with isotropic mesophase.
Region E   mesophase with middle soap structure.
    » L_1 with isotropic aqueous micellar solution.

DISCUSSION

The regions of existence of the isotropic mesophases whose presence has been demonstrated in this study lie in quite different parts of the triangle diagrams for the ternary systems. Five of them are in equilibrium with aqueous

Table 5. Isotropic mesophases in systems of sodium caprylate — chlorinated hydrocarbon — water.

Composition %			Bragg spacing Å	Intensity	hkl if primitive cubic lattice	if body-centred cubic lattice
NaC_8	1-Chloro-octane	Water				
42	7	51	39.2	weak	200	220
			34.6	medium	210	310
			31.6	medium	211	222
			29.1	faint	220	321
			17.3	weak	420	620
					$a_0 = 77.5$ Å	$= 109$ Å
38	Tetrachloro-methane 7	55	38.0	weak	200	220
			32.1	medium	210	310
			29.2	medium	211	222
			15.4	weak	420	620
					$a_0 = 72$ Å	$= 102$ Å

solutions in region L_1 and another extends from the soap-water axis, but is separated from the regions of existence of the solution L_1 by another mesophase. The others lie nearer the middle of the diagram, quite remote from the soap—water axis; one of them is in equilibrium with the isotropic solutions in an organic solvent in region L_2, while the second is separated from this region by another mesophase.

Among the isotropic mesophases considered here the normal as well as the reversed and complex structures would seem to be represented. In the system in which both normal and reversed structures were found they lay on each side of a mesophase region with a lamellar structure, the normal one on the side with the greater amount of water. Complex spherical structures have as a rule tended to lie nearer the middle of the ternary systems, at sites where they may well be regarded as a stage in the transformation to a lamellar structure; this is particularly clear in the oleate system.

This position of the isotropic mesophases is consistent with other aspects of the behaviour of "normal" and "reversed" mesomorphous particle structures in ternary systems. For instance, the former have hitherto always been found at a higher water content than that of the lamellar mesophase with which they are in equilibrium, while the reversed structures have been observed definitely only at a lower water content; complex structures, on the other hand, would seem to occur on each side of the lamellar mesophase.

As is evident from the above, the proposed structural models are tentative, and further examination by different experimental methods is required. It may be mentioned that e.g. recent work by Luzzati and coworkers has presented new ideas on the structure of the cubic phases in non-aqueous and water-poor amphiphilic systems.[21,22]

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