

MICELLAR SIZE AND SURFACE ACTIVITY OF SOME C₁₈ α-MONOGLYCERIDES IN BENZENE

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Some C₁₈ α-monoglycerides in benzene have been studied by the light-scattering and surface tension methods. The glycerol esters of stearic, oleic and linoleic acids had micellar weights of less than 7,000; glycerol monoricinoleate had a micellar weight of over 18,000. All the monoglycerides showed some surface activity in benzene, glycerol monoricinoleate having the greatest, the other unsaturated monoglycerides the least.

A CHARACTERISTIC of surface-active substances is the presence of both hydrophilic and lipophilic regions in the molecule. The hydrophilic region will be polar or ionic and the lipophilic region a relatively non-polar hydrocarbon chain or ring. The balance between the hydrophilic and lipophilic regions can be varied in several ways.

In biological systems substances possessing surface activity are numerous. Among the more important are the lecithins and monoglycerides—the latter can be regarded as non-ionic *in vivo* whilst the former possess a zwitter-ion structure and are non-ionic only at their isoelectric points. Both these types may possess saturated and unsaturated fatty acid components which will in turn vary the extent of solubility in aqueous and non-aqueous systems. The double bonds will modify the lipophilic region of a molecule and consequently its surface activity. This is important in biological systems where these substances play an active role in solubilisation and transportation of lipids.

The effect of double bonds on the micellar size and surface activity of some C₁₈ α-monoglycerides has been investigated. The influence of an hydroxyl group, in the hydrocarbon chain of ricinoleic acid, on the surface activity of glycerol monoricinoleate was also examined.

EXPERIMENTAL

Preparation of the α-Monoglycerides

The stearic, oleic, linoleic and ricinoleic monoesters of glycerol were prepared by a method similar to that of Averill, Roche and King¹. The fatty acid chlorides were first prepared by slowly adding 0.06 mole of fatty acid to 0.18 mole of oxalyl chloride and refluxing for 4 hours in an all-glass still. Excess oxalyl chloride was removed at 2–3 mm. pressure.

Acetone-glycerol was prepared by reacting 100 g. freshly distilled anhydrous glycerol with 200 ml. acetone saturated with dry hydrogen chloride over fused anhydrous sodium sulphate. The acetone-glycerol was purified by shaking with excess lead carbonate to remove hydrogen chloride, filtered and dried over anhydrous sodium sulphate.

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The acetone-glycerol α -ester compounds were prepared by mixing equimolecular proportions of acetone-glycerol and quinoline in a 25 ml. round-bottomed flask immersed in an ice-cold bath. An equimolecular quantity of cold fatty acid chloride was added and the mixture allowed to stand for 2 days. 25 ml. of ether and 1.0 ml. ice-cold 0.5N sulphuric acid were added to the mixture, shaken in a separating funnel and the acid layer drawn off. The ether layer was shaken several times with 5 ml. portions of sodium bicarbonate solution and washed well with water. The solution was then dried over anhydrous sodium sulphate and filtered.

The protecting acetone group was removed from the α -ester by cooling an ethereal solution of the ester in an ice-cold bath and slowly adding 5 ml. 10 N sulphuric acid. After 30 minutes 15 ml. water was added and the

TABLE I
REFRACTIVE INDEX INCREMENTS FOR α -MONOGLYCERIDES

Monoglyceride	M.p.	I.no.	Refractive index	dn/dc	Monomer weight	Micellar weight
Monostearate	81.8°	—	—	0.0634	358.5	4,730
Monooleate	35.8°	70.3	1.4625 (40°)	0.0658	356.5	6,900
Monolinoleate	12.5–14°	142.0	1.4767 (20°)	0.0520	354.5	5,400
Monoricinoleate	5°–6°	67.7	1.4717 (20°)	0.0654	372.5	18,600

contents placed in a freezing mixture when the monoglycerides separated out. The stearic ester was washed, dried over anhydrous sodium sulphate and crystallised from a mixture of 1:1 ether and light petroleum. The unsaturated esters were treated in a similar way but crystallised over a longer period of time and at a much lower temperature.

Preliminary light-scattering experiments with the α -monostearate showed that traces of free fatty acid considerably increased the scattered light. Adequate washing of an ethereal solution of the monoglycerides with sodium bicarbonate solution and water was carried out to ensure the complete absence of hydrolysis products.

Apparatus

The light-scattering instrument constructed in our laboratory and based on that designed by Hughes, Johnson and Ottewill² has been described³. Subsequent modifications to the apparatus have also been reported⁴. All measurements were made with the mercury green line, $\lambda = 5,461 \text{ \AA}$. Ludox was used as a calibrating liquid.

The specific refractive index increment was determined by means of a Rayleigh interference refractometer modified for monochromatic light as described by Bauer⁵. All measurements were taken at 20°.

Surface tensions were measured by the ring method using the chainomatic balance assembly previously described⁶.

All measurements were taken at 20°.

RESULTS AND DISCUSSION

Light-Scattering

The refractive index increments for the α -monoglycerides are given in Table I.

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The scattering intensity at 90° was corrected for solvent effects and plotted in terms of Kc/R_{90} against concentration for comparison with Zimm's basic scattering equation⁷,

$$\frac{Kc}{R_{\theta}} = \frac{1}{MP(\theta)} + 2Bc$$

where K contains optical constants of the scattering system ;

c = concentration of monoglyceride g.ml.⁻¹;

R_θ = reduced intensity of the scattered light at angle θ;

B = interaction constant;

M = molecular weight; and

P(θ) = particle scattering factor to correct for internal interference.

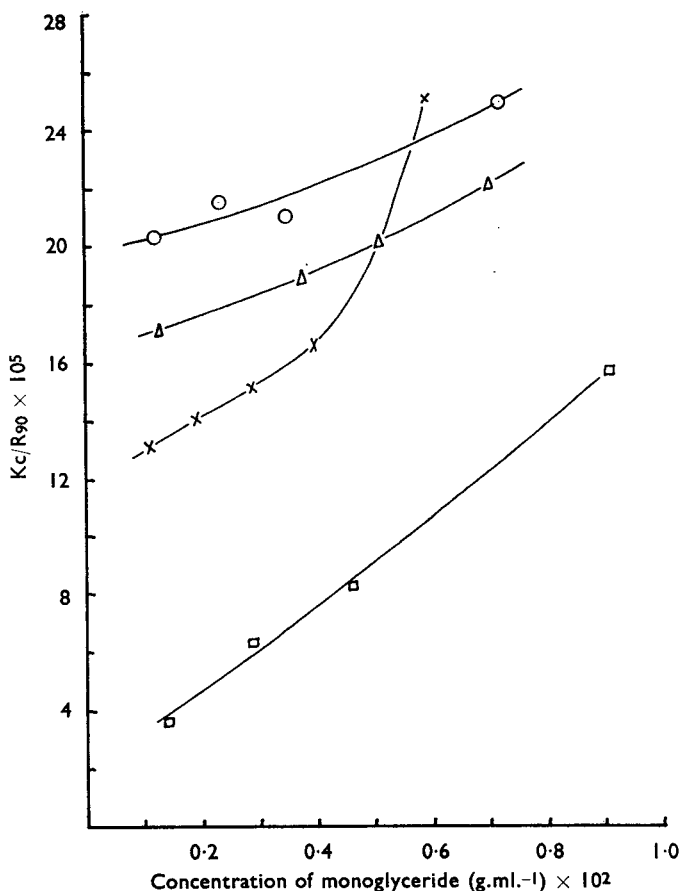


FIG. 1. 90° scattering curves for the α-monoglycerides in benzene at 20° C.

○ Monostearin × Monoolein △ Monolinolein
 □ Monoricinolein

Since micelles and not single molecules contribute to the scattering of light, Debye⁸ has suggested that the concentration term should be $c - c_0$ where c_0 is the concentration of monomers (critical micelle concentration). The light scattered by the particles was, however, so small that a critical micelle concentration was not measurable. For a similar reason values for the molecular weight were not obtained by extrapolation but by averages of the values of Kc/R_{90} in the more dilute region (below 0.5 per cent w/v).

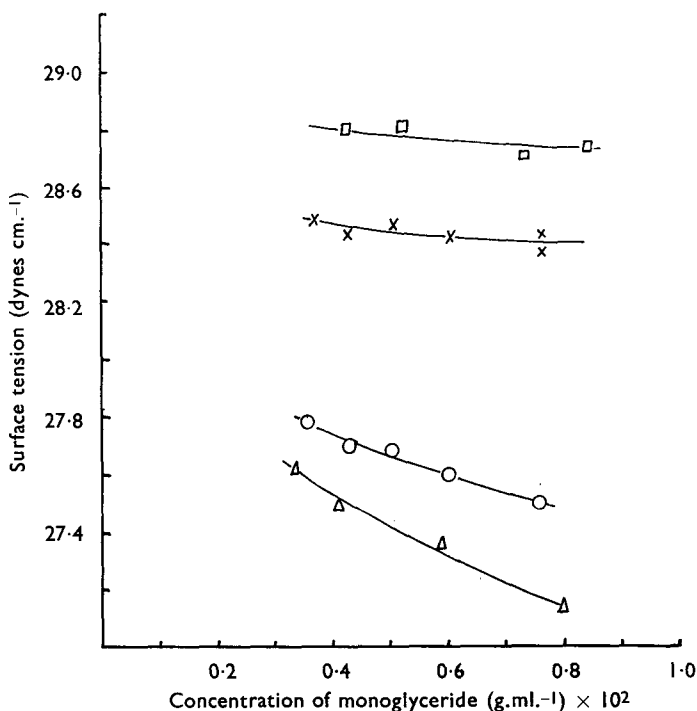


FIG. 2. Surface tension effects of some α -monoglycerides on benzene at 20° C.

○ Monostearin × Monoolein □ Monolinolein
 △ Monoricinolein

The depolarisation of scattered light after correcting for solvent effects was small (less than 0.04) for all the monoglycerides.

The dissymmetry of scatter at 30° either side of 90° to the incident beam was never greater than 1.05 and on account of the low level of scatter the contribution of dust particles towards this value may have been significant.

The monoglycerides form dispersions in water but are soluble in benzene. From the dual character of the monoglyceride molecules they would be expected to form micelles in a non-aqueous solvent having a long-chain hydrocarbon periphery surrounding the hydrophilic glycerol nucleus, that is, "inverted" forms of the classical soap micelle.

SURFACE ACTIVITY OF C₁₈ α-MONOGLYCERIDES

The monostearate particles were the smallest of the four glycerides examined and contained approximately 13 monomers per micelle (Fig. 1). Introduction of a double bond into the hydrocarbon chain resulted in a larger particle size formation shown by glycerol monooleate. It is possible that monooleate is slightly less soluble than monostearate which would have resulted in the formation of larger aggregates; the polar effect of the double bond in the hydrocarbon chain may also have influenced the orientation of the long chains in micelle formation.

Results obtained from the light scattered by monolinoleate particles differed from those expected from a further increase in polar character of the long-chain fraction (two double bonds) of the glyceride molecule. The dissymmetry of scattering was very low and the possibility of increased scatter arising from impurities was negligible. It was first suspected that hydrolysis may have occurred producing some free fatty acid which contributed to the increased scatter; furthermore, some solubilisation of the free glycerol within the micelles could also have increased the scatter. Repetition of the sodium bicarbonate purification treatment did not produce any substantial change in scattering. The smaller particle size was then attributed to a closer but probably more complex packing of the hydrocarbon chains.

The presence of an hydroxyl group in the long chain made a significant increase in size of the micelles shown by the scattering from glycerol monoricinoleate. Due to this hydroxyl group the ester would have a lower solubility in benzene than the other monoglycerides and the formation of larger aggregates could be expected. The hydroxyl group was also likely to hinder the orientation of hydrocarbon chains to a close packing in the micelles.

All the monoglycerides showed some surface activity in benzene (Fig. 2). The lowering of the surface tension of benzene by monooleate and monolinoleate was very small and less than that shown by monostearate. They are all soluble in benzene but the presence of a polar region at the double bonds of the unsaturated monoglycerides appeared to decrease their surface activity. The large micellar size of monoricinoleate calculated from the light-scattering measurements was partly attributed to it being less soluble in benzene. The hydroxyl group present in monoricinoleate showed a greater tendency to orient itself in the surface layer, again due to the solubility relationship, away from the hydrocarbon solvent, so bringing about a greater lowering of the surface tension.

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