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Studies on the Energy Barrier to Mesophase Transformations in Lyotropic Liquid Crystalline Systems

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Studies on the mesophase transformations exhibited by supersaturated aqueous solutions of four different lithium sulfoacetate esters were carried out. The concentration changes required to bring about these transformations in a population of non-communicating droplets were created by selective extraction of water from each of them into the support medium. By analogy with crystal nucleation from solution, it was concluded that the stochastic nature of the transformations must be a result of an energy barrier. The magnitude of each energy barrier was not estimated because appropriate reference points are not available.

INTRODUCTION

The question about an energy barrier to mesophase transformations in lyotropic liquid crystalline systems seems to be unresolved. We have found only one statement on the matter, that by Winsor: "The possibility of such metastability in course of the transformation between liquid states is of much interest and is difficult to interpret."[1]. Here, he is commenting on the supercooling behavior exhibited by N,N,N,-trimethylamminododecanoimide–water for the $G \rightarrow V_1$ transformation.[2]

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Metastability, on the other hand, is a general phenomena observed during transformations between gas–liquid, liquid–solid and solution–crystal phases. In models of the nucleation event, the energy barrier which gives rise to this metastability is a direct result of the necessary embryo buildup, configurational requirements, desolvation and the formation of a surface all of which distinguish the newly forming phase from the supersaturated host phase. The magnitude of the energy barrier is estimated from the supersaturation, calculated using the equilibrium state between the two phases (e.g., the equilibrium solubility of a crystalline solute) as a reference point, and σ, the surface free energy of the forming phase. Phase changes between the transient but characteristic structures proposed for the various lyotropic liquid crystalline mesophases may have similar requirements of embryo size, configuration and desolvation. And these could give rise to an analogous energy barrier to transformations from one phase to another. Price has reported such a barrier to mesophase transformations in certain thermotropic systems.[3]

Recently, we found evidence which forced the conclusion that there must be an energy barrier to mesophase transformations in two lithium sulfoacetate ester–water systems. In this paper we report and discuss the results obtained when preferential extraction of solvent into an immisible support medium from non-communicating aqueous droplets was used to create concentration change in the droplet population. Observations on the nature of each mesophase and the transformations between them were made photomicroscopically under crossed polars.

EXPERIMENTAL DETAILS

Reagents

The four esters, lithium *p*-bromobenzylsulfoacetate, lithium *p*-nitrophenacylsulfoacetate, lithium *p*-nitrobenzylsulfoacetate and lithium *p*-bromophenacylsulfoacetate were synthesized using a method adapted from that described in Shriner, Fuson and Curtin[4]. Saturated solutions of each of them were prepared by gently warming excess ester in water with stirring. The solutions were then allowed to stand for at least one day in contact with the remaining solid. Just before use the solutions were pressure-filtered through a 0.3 μ PVC membrane filter. Various silicone fluids of the 200 series (Dow Corning, Toronto) were used as the supporting medium.

Apparatus

The dispersions were prepared by means of a Virtis microhomogenizer (Fisher

Scientific) then poured into specially made observation cups. The cups were made by fusing 28 mm diameter optically flat Pyrex discs onto Pyrex glass tubing, 28 mm x 25 mm. The containers were made hydrophobic by coating the inside surfaces with Drifilm SC-87.

The dispersions were viewed and photographed using a Vickers M15 polarizing microscope (magnification 75X) equiped with an Autowind 35 mm camera. The microscope was built on an optical bench and set up for Kohler illumination using 500-watt super-high pressure mercury vapour lamp. The microscope was equipped with a micrometer stage and a removable cell holder for the observation cup. An accurate micrometer having a range 0.01 to 20 mm was mounted on this stage. This allowed the sequential observation of several fields of view and ensured subsequent precise relocation of each.

Photomicrographs were taken using Anscochrome D-500 colour reversal film and an Autoexposure unit J-35 modified to allow control of shutter speed for the dark field exposures.

A dry atmoshere was maintained by directing a gentle stream of clean, dry compressed air into the observation cup by means of four polyethylene tubes mounted around the objective lens of the microscope.

The film slides were viewed with a Leitz Paradovit projector equipped with a 150 mm lens and a projection screen ruled in millimeters.

Procedure

One or two drops of the appropriate ester solution[†] were stirred in 5 ml of D.C. 200-20 c.s. oil for 5 seconds at 25000 r.p.m., then transferred to a standard 15 ml centrifuge tube containing 9 ml of D.C. 200–100 c.s. oil. The tube was centrifuged for 1 minute at 4000 r.p.m., then 2–3 ml were removed with an eye dropper from the middle of the tube and poured onto a thin film of the same oil in an observation cup. This was centrifuged for 30–60 seconds. The supernant oil was decanted, replaced with fresh D.C. 200–100 c.s. oil to a depth of 3 mm and then centrifuged for 30 seconds.

The observation cup was inserted into the cell holder and fitted on the microscope stage and then a suitable region was selected for observation. Usually 5 or 6 adjacent fields of view were recorded[‡], each being less than 3 mm away from the central field of view.

[†] In all cases except lithium p-bromophenacylsulfacetate saturated solutions were used. Solutions of this ester were 90% saturated.

[‡] To record the liquid crystalline mesophase changes within the droplet population photomicrographs (crossed polars) were taken at 1 minute intervals using a 10% N.D. filter and 1/2-second exposure. To record the change of droplet size within the population, photomicrographs were taken using unpolarized light at regular intervals (usually 5 minutes) using a 0.1% N.D. filter with 1/2-second exposure.

After processing and sorting, the slides were projected in turn on the ruled screen. The individual droplet diameters were measured and the times of the transitions to the various liquid crystalline mesophases were recorded.

The droplet diameters were converted to microns using a scale factor determined by calibrating the ruled screen with a photomicrograph of a millimeter slide taken at the same magnification factor.

RESULTS AND DISCUSSION

Qualitative observations

In the discussion which follows the experimental observations for the phase changes within each droplet of the population will be illustrated for the case of lithium *p*-bromobenzylsulfoacetate. Differences for the other esters will be noted later.

Droplets prepared from a saturated solution of lithium *p*-bromobenzylsulfoacetate dispersed in a silicone fluid were observed to go through a series of optical changes as the concentration of the ester contained within each of them increased as a result of extraction of water into the supporting medium. Photomicrographs of the droplets illustrating these changes are included in Figure 1. Each frame represents the same field of views at increasing degrees of supersaturation.

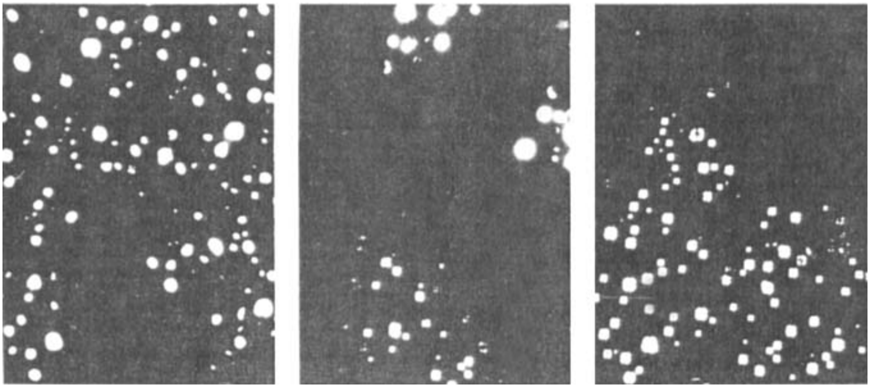


FIGURE 1 Photomicrographs illustrating the three liquid crystalline phases of the lithium *p*-bromobenzylsulfoacetate solution under crossed polars.

Initially the droplets are clear and isotropic to polarized light (not shown), then with only a slight increase in supersaturation they transform to the first birefringent phase. This phase is evident in Figure 1a which shows that the droplets shine brightly and exhibit random interference patterns. As the supersaturation increases, the droplets extinguish and again become isotropic. This is apparent in some regions of each frame in Figure 1. Note that there is a gradient of increasing concentration from left to right in the field of view. As the concentration continues to increase, the droplets become birefringent again, but in this case, each droplet displays the same interference figure, the Maltese cross, as seen in Figure 1c. Further increase in supersaturation leads to the instantaneous collapse of the droplet into an irregular mass of crystals (not illustrated).

Under unpolarized light the droplets remain completely clear until the moment of crystallization. This is illustrated for the same field of view in Figure 2. Figure 2a is the first of a series of photomicrographs which were used to measure the rate of change in supersaturation. Most of the droplets in this

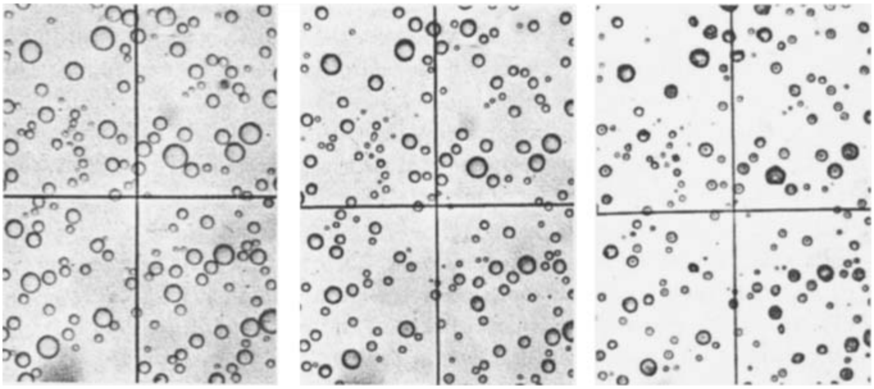


FIGURE 2 Photomicrographs of the lithium *p*-bromobenzylsulfoacetate droplets under transmitted light at the start, midway and near the end of an experiment.

frame, if viewed with polarized light, would exhibit the birefringence effects shown in Figure 1a. Figure 2b corresponds to Figure 1b, being taken one minute later. It is seen that while all the droplets were distinguishable under unpolarized light, they are not under polarized light. Figure 2c shows the droplet population at a later time when crystallization has begun. The crystallized droplets are clearly distinguishable as dark masses. Those droplets which remain uncrystallized, although clear to unpolarized light, would, under crossed polars, display the Maltese cross of Figure 1c.

In the case of lithium *p*-nitrobenzylsulfoacetate and lithium *p*-nitrophenacylsulfoacetate, only one phase was observed prior to crystallization. The droplets transformed directly from the isotropic liquid to the anisotropic phase displaying the Maltese cross. For lithium *p*-bromophenacylsulfoacetate two birefringent mesophases formed which were not separated by an isotropic phase. The two birefringent phases appeared in the same order and showed the same interference patterns as those of lithium *p*-bromobenzylsulfoacetate.

Interpretation of the qualitative observations

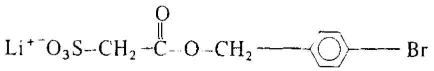
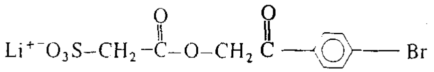
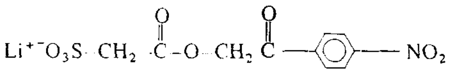
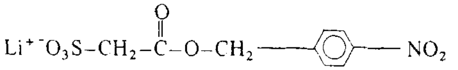
The Maltese cross is the characteristic interference pattern of a uniaxial crystal aligned with the line of view coincident with its optic axis. Such a pattern is well known for spherulities in which a spherical crystal is built-up in concentric layers.[5] In this case any diameter of the sphere corresponds to a normal to the layers and would be an optic axis. Thus, for the liquid crystalline phase displaying this cross, an onion-like arrangement of micellar layers would account for the observed interference pattern. The layered structure of this mesophase then, is analogous to the "neat" phase or "G" phase of aliphatic soap systems.

Having established the G phase as a reference point the other phases observed can be assigned according to the scheme presented by Winsor (Ref. 1, Figure 2). That is, the first birefringent phase, which occurs at the lowest concentration, would correspond to the M_1 phase and the isotropic intermediate mesophase, to the V_1 phase. An arrangement of parallel micellar rods, the M_1 phase, could result in interference patterns associated with a uniaxial crystal. If the optic axis were coincident with the microscope axis, then an interference pattern resembling the Maltese cross would be observed. Other aligments would result in other interference patterns. In figure 1a a few droplets exhibit the Maltese cross, others shine uniformly but in most cases the isogyres of the cross are separated. The intermediate phase is isotropic, an observation consistent with the expectations for the V_1 phase. A summary of the mesophases exhibited by each of the four lithium sulfoacetate esters is shown in Table I.

The existence of the above mesophases could not be confirmed by observation of their characteristic textures using peripheral evaporation of a thin film of solution because each occured at concentrations higher than the equilibrium

TABLE I

Mesophases exhibited by each of the lithium sulfoacetate esters.

Compound	Mesophases
(1) 	Solution → M_1 → V_1 → G → crystals
(2) 	Solution → M_1 → G → crystals
(3) 	Solution → G → crystals
(4) 	Solution → G → crystals

solubility of the solid. Thus, crystals formed at the boundary and simply acted as growth centres. The droplet technique, by sequestering the effect of heterogeneous catalysts, prevented crystallization and consequently enabled these phases to form.

It should be noted from the data of Table I that at least three series of mesophase transformations were observed for the lithium sulfoacetate esters. The esters are listed in the Table in order of increasing intermolecular interactions of the lipophilic "end" group. This increasing interaction could account, in part, for the absence of the M_1 mesophase in both of the nitro derivatives. Compared with the lamellar micelle of the G mesophase the micellar rods of the former mesophase would be less stable with increasing interaction because of closer packing of the lipophilic groups. The absence of the V_1 mesophase in the lithium *p*-bromophenacylsulfoacetate series and possibly from the series for each of the nitro derivatives remains unexplained.

Transformations to the mesophases

Generally, by analogy to the crystallization of a solid, a metastability of the initial mesophase relative to the forming mesophase might be anticipated. In this study there is a problem of how this metastability should be defined. As has been stated above, the saturated solutions of these compounds do not exhibit liquid crystalline character, only the unstable supersaturated solution is mesomorphic. Thus, the problem is how to decide, in the absence of an equilibrium reference concentration, whether or not there is any metastability prior to liquid crystal transformations. For the case of crystal nucleation from solution [illegible] stochastic process] a distribution of the number of droplets crystallized as a function of concentration is obtained because of the energy barrier to the transformation[6,7,8,9]. If within our droplet population there is a distribution of the number of droplets transformed to a mesophase as a function of concentration, then it can be reasoned, by analogy, that the initial phase is metastable with respect to the newly forming phase.

The results for transformations to various mesophases for the cases of lithium *p*-nitrophenacylsulfoacetate and lithium *p*-bromobenzylsulfoacetate are presented in Table II. For the range of supersaturations[†] over which these transitions occurred the experimental error is about 0.1 units. Thus, there is some doubt in the case of lithium *p*-nitrophenacylsulfoacetate that the spread of values over the narrow supersaturation range is in fact a distribution due to metastability of the isotropic solution.

TABLE II

Supersaturation ranges over which transitions to the liquid crystalline mesophases occurred

Compound	3[a]	1[a,b]	
supersaturation[c] transition	$S \rightarrow G$	$M_1 \rightarrow V_1$	$V_1 \rightarrow G$
1.0	0	0	
1.1	189	2	
1.2	145	70	0
1.3	16	176	24
1.4	2	175	150
1.5		43	202
1.6		8	70
1.7		2	22
1.8		0	5
1.9			3
Total number of droplets examined	352	477	477

[a] For compound identification see Table I.

[b] The transition $S \rightarrow M_1$ was well underway within the droplet population before it was possible to record its progress so that the question about any associated metastability could not be answered.

[c] The supersaturation was calculated from the ratio: concentration of solute within the droplet at the detection of the mesophase transformation/equilibrium solubility of the crystalline solute.

[†] Here the equilibrium solubility of the solid is still the reference point since the equilibriun concentration for the existence of the mesophase is unknown.

The distributions for the $M_1 \rightarrow V_1$ and the $V_1 \rightarrow G$ transformations in the case of lithium *p*-bromobenzylsulfoacetate are more significant. Here the spread of supersaturation values for each of the transitions is greater than the breadth of the experimental error. Consequently, we must conclude that the M_1 and V_1 mesophases exhibit metastability prior to transformation. Evaluation of the magnitude of the energy barrier to each of these transformations awaits evaluation of the appropriate reference points, i.e., the respective concentrations where each one of the two pairs of mesophases is in thermodynamic equilibrium. The schematic diagram, shown as Figure 3, summarizes our interpretation of the behaviour exhibited by supersaturated solutions of lithium *p*-bromobenzylsulfoacetate.

Acknowledgement

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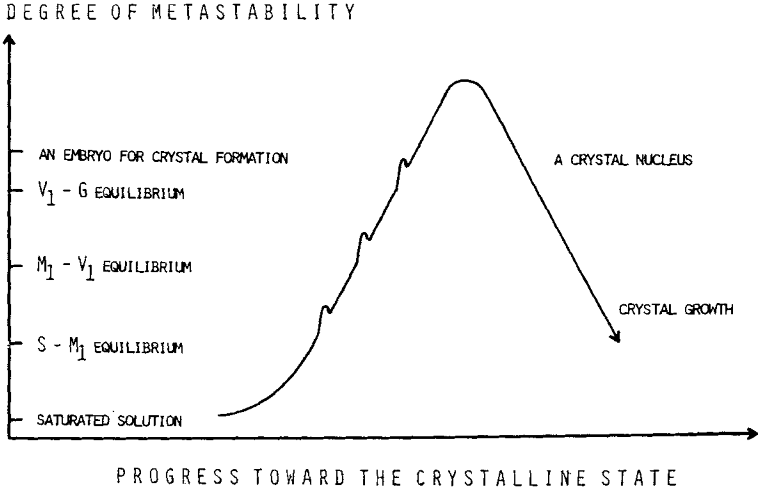

FIGURE 3 Schematic representation of the degree of metastability, using the saturated solution as a reference point, associated with various phase equilibria for lithium *p*-bromobenzylsulfoacetate.

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