Potential of Reflectance Anisotropy Spectroscopy (RAS) for Mapping the Anisotropy of Lyotropic Liquid Crystal Dispersions in Formulations

E M Prescott, K L Rabone, C I Smith and P Weightman
Department of Physics, University of Liverpool

Abstract

The anisotropy of binary mixture of an anionic surfactant Aerosol OT (AOT) and glycerol (used as a model for water) was investigated using Reflectance Anisotropy Spectroscopy (RAS). The variation in the measured anisotropy parallels the expected behaviour of a dispersion of lyotropic liquid crystals as a function of concentration and temperature. A response surface of anisotropy as a function of temperature and surfactant concentration demonstrates the potential for RAS as a tool for mapping liquid anisotropy to assist formulation.

1. Background

1.1 Lyotropic liquid crystal dispersions in formulations

Lyotropic liquid crystals are well known [1, 2]. Lyotropic liquid crystals form when amphiphilic anisotropic molecules (that is, molecules that are hydrophobic at one end and hydrophilic at the other) self-assemble in both polar and nonpolar solvents.

In formulation studies, phase boundaries apparently seen for lyotropic liquid crystals can be the result of kinetically stable artefacts caused by the self-suspension of dispersions as the viscosity of the formulation increases [3]. Evidence for this effect is provided by fast freezing coupled with electron microscopy when submicron lamellar phase droplets may be clearly observed [4].

Lyotropic liquid crystal dispersions at the submicron level have commercial value across a wide range of applications including fabric washing, fabric care (softening), hard surface cleaning, (including dental care) and have potential for the delivery of pharmaceuticals.

Lyotropic liquid crystal dispersions are often formulated by the self-assembly of a mixture of anionic and nonionic surfactants in the presence of electrolytes to provide the desired rheological control (or "structuring") of liquids or pastes. Desired rheological properties include: the ability to dynamically suspend minerals such as calcite and silica abrasives with particle sizes in the tens of microns in highly shear-thinning liquids; suspension of surfactant in liquids for washing and softening fabrics; adding "cling" to hypochlorite solutions for cleaning toilet bowls.

The rheological properties of liquid crystal dispersions may be characterised by a flow curve, a plot of viscosity against shear rate, and are ultimately derived from the alignment of anisotropic units in a shear field.

1.2 Anisotropy

Lyotropic liquid crystals form thermodynamically stable phases which are mostly anisotropic structures (for example, hexagonal phase or lamellar phase). When lyotropic liquid crystals are viewed between crossed polarisers in polarised light microscopy, textures are seen which may be used to characterise the different phases formed [2, 5].

1.3 Reflection Anisotropy Spectroscopy (RAS)

RAS is a relatively recent optical technique which also relies on polarised light [6]. Derived from spectroscopic ellipsometry, RAS is designed to operate in the visual/UV spectral range (225 – 825 nm, 1.5 – 5.5 eV) but applied at normal incidence. This results in a much less model dependent analysis of spectra, particularly for the determination of film thickness which is simply proportional to the RAS signal strength.

In principle, RAS provides a means for quantifying the degree of anisotropy of a formulation and for mapping the anisotropy of formulation space as a function of composition and temperature. The anisotropy observed by RAS could therefore be a useful parameter for formulation optimisation.

2. Aim of Work

The aim of this work was to explore the possibility of using RAS to map the changes in the degree of anisotropy of solutions of a single surfactant, di-octyl sulphosuccinate in glycerol, held between microscope coverslips, as a function of temperature. Two-tailed di-octyl sulphosuccinate is known to form lyotropic liquid crystals in glycerol [7].

3. Materials and Methods

3.1 Materials

Sodium bis (2–ethylhexyl) sulfosuccinate (Figure 1 below) was obtained as Aerosol OT (AOT) from Sigma–Aldrich (99 per cent purity).

Glycerol was also obtained from Sigma-Aldrich and used as received.

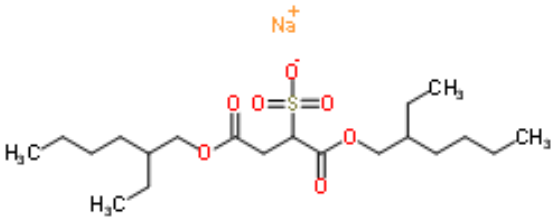


Figure 1 Sodium bis (2–ethylhexyl) sulfosuccinate

3.2 Methods

Solutions of AOT in glycerol were prepared by weighing and stirring overnight with a magnetic bar rotating at 150 rpm at a temperature of 60 Celsius to ensure complete dissolution. Concentrations of 30, 40 and 50 weight per cent of AOT in glycerol were prepared.

The solutions were examined to confirm optical anisotropy using a Leitz polarising light microscope equipped with a JVC digital camera. The microscope was used in the transmission mode with a magnification of 320 with the solutions contained between cover slips (BDH, borosilicate, 18 mm x 18 mm, thickness No. 1).

Reflectance spectra of these solutions were obtained as a function of wavelength in the range 1.5 - 5.5 eV and as a function of temperature (23 – 50 Celsius). The RAS instrument used followed the Aspnes design [18] and was equipped with a xenon arc light source. The solutions were contained between quartz cover slips placed on a Linkham LT 350 heating stage equipped with a Linkham TP 93 temperature monitor. The heating stage and sample were aligned with the beam. The lower cover slip was painted on the underside with heat resistant black paint (Hycote) to minimise back scattered light. Samples were rotated in the horizontal plane to obtain the optimal orientation for the maximum signal which was found to be at 4.7 eV (264 nm). A control using just glycerol showed a relatively flat, featureless spectrum.

4. Results and Discussion

4.1 Qualitative Optical Anisotropy

The work of Petrov *et al* (7) has demonstrated the existence of a region of lamellar phase for solutions of 30 to 50 per cent AOT in glycerol in the temperature region 20 to about 50 Celsius. Microscopic examination of our solutions of 40 and 50 per cent AOT in glycerol using polarised light at 25 Celsius clearly showed the features characteristic of lamellar phase – oily streaks and "Maltese" crosses. These features disappeared as the 40 per cent sample was heated to 40 Celsius and became isotropic as the phase melted.

4.2 Quantitative Measurement of Anisotropy

The anisotropy of the 3 concentrations of AOT was measured at 4.7 eV (264 nm) at 25, 30, 40 and 50 Celsius. The results are tabulated below.

Table 1

Variation of Anisotropy with Temperature and Concentration of AOT

AOT	Temp	Anisotropy
30	25	0.3857
30	30	-0.019
30	40	0.1298
30	50	0
40	25	4.254
40	30	0.2919
40	40	-0.25
40	50	0
50	25	16.369
50	30	11.635
50	40	0.5759
50	50	0

The variation of anisotropy with temperature and concentration of AOT gratifying shows the changes expected; the anisotropy tends the fall as the temperature is increased and tends to increase with concentration. The variation was subjected to a statistical analysis of variance using the JMP statistical software (9). The results of the analysis are shown in Table 2 below.

Table 2

Analysis of Variance of Anisotropy

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	5	303.09585	60.6192	13.9066
Error	6	26.15419	4.3590	Prob>F
C Total	11	329.25004		0.0030

The analysis of variance shows a highly significant variation of the measured anisotropy with temperature and concentration (99.7 per cent confidence). The data was further analysed to obtain the response surface of the variation of anisotropy with temperature and concentration of AOT.

Table 3

Response Surface Analysis of Anisotropy as a function of Temperature and Concentration of AOT

Summary of Fit

R Square	0.920564
R Square Adjusted	0.854368
Root Mean Square Error	2.087829
Mean of Response	2.781025
Observations	12

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	11.694536	25.93577	0.45	0.6679
AOT	-0.463803	1.062678	-0.44	0.6778
Temp	-0.224145	0.765077	-0.29	0.7794
AOT*AOT	0.0256058	0.012785	2.00	0.0921
Temp*Temp	0.017374	0.009282	1.87	0.1104
AOT*Temp	-0.034031	0.007688	-4.43	0.0044

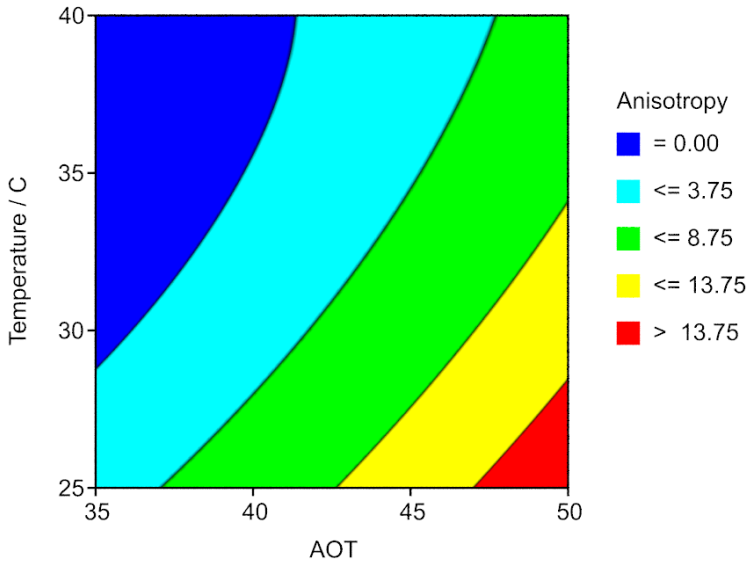
Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
AOT	1	1	0.830336	0.1905	0.6778
Temp	1	1	0.374144	0.0858	0.7794
AOT*AOT	1	1	17.484118	4.0110	0.0921
Temp*Temp	1	1	15.271887	3.5035	0.1104
AOT*Temp	1	1	85.409260	19.5936	0.0044

The response surface analysis clearly shows the effect of the strong interaction between temperature and AOT concentration on the anisotropy. Using the parameter estimates a smoothed response surface was constructed for positive values of the anisotropy using the POV-Ray drawing software (10). The response surface is shown below as Figure 2.

Figure 2

Response Surface of the Anisotropy of AOT in Glycerol as a function of Temperature and Concentration (per cent)



5. Conclusions

This model study has demonstrated the feasibility of using quantitative measurements of anisotropy using RAS to assist formulation studies. The response surface shows the boundary between isotropic solutions and solutions that contain lyotropic liquid crystal phases. Moreover, boundaries between different regions of anisotropy are likely to be related to the concentration of the LLC phase and could therefore assist a formulator to define a suitable concentration to achieve a desired effect such as the suspension of solids.

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7. References

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10. POV-Ray, Persistence of Vision Raytracer, http://www.povray.org/