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Birefringence of Smectic Modifications of the Homologous Thallium Soaps†

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Abstract—The birefringence has been studied of the smectic high temperature modification (neat phase) of the anhydrous thallium soaps in dependence on temperature and at different wavelength. The measurements were carried out on uniaxially orientated liquid crystalline layers on the principle of Abbé's double prism. The lower homologues exhibit negative double refraction which decreases with increasing chain length and decreasing temperature. In the middle members of the homologous series a change in the sign of double refraction is observed. The higher members exhibit positive birefringence, which increases with increasing alkyl chain length and with decreasing temperature. An attempt will be made to explain this behaviour on the basis of the structure of the smectic modification of the thallium salts.

1. Introduction

As part of the extensive investigations of the double refraction of liquid crystalline smectic modifications(1,2) we have also studied the double refraction of the neat phases of anhydrous thallium soaps. The morphological connections of the neat phase with the smectic modifications of aromatic compounds have recently been described.(3) The knowledge of the structure of these phases especially through the works of Luzzati, Skoulios and coworkers(4,5,6,7) allows a more detailed discussion of the results. The thallium salts were selected for measurement because of the favourable temperature range of the liquid crystalline state.

2. Substances

The anhydrous thallium salts of *n*-fatty acids were synthesized according to the formula of Holde and Selim.(8) The microscopically

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determined transition temperatures are to be found in Table 1 together with the values of Walter, who first investigated the liquid crystalline behavior of these compounds.(9)

The smectic high temperature modification of the thallium salts between slide and cover slip appears mostly as an optically uniaxial pseudoisotropic texture. Under suitable conditions a well-formed, fan-shaped texture is also obtained.(11)

TABLE 1 Transition Temperatures of Thallium Salts

	Transition into the neat phase		Clearing point	
n†	This work	Walter	This work	Walter
5	181.0	175.0	215.5	212.0
6	149.0	152.0	229.5	224.0
7	142.8	143.0	227.5	227.0
8	135.7	136.0	222.5	220.0
9	138.6	130.0	217.0	215.0
10	131.0	127.0	209.5	207.0
11	130.4	126.0	203.5	201.0
12	124.7	123.0	197.0	197.0
14	120.2	119.5	185.0	181.5
16	118.2	116.0	175.5	172.0
18	119.0	118.0	167.0	163.0

† n = number of C-atoms.

3. Method of Measurement

Measurements of refractive indices were carried out on optically uniaxial layers on the principle of Abbé's double prism. Further details about the refractometer used and the measuring method are reported in another place.(1,2) Measurements were carried out at four wavelengths: 436, 546, 589, 644 nm. The average error of the measured refractive indices amounts to about $\pm 1.10^{-3}$. At higher temperatures the average error of measurements is larger because substances decompose a little. Some of the lower homologues begin to sublime at about 180 °C which renders measurement more difficult.

4. Results of Measurements

A summary of the measured results are given in Tables 2–12. The refractive indices at the temperatures listed are taken from the refractive index-temperature-curves obtained by the graph-balancing method from the single values.⁽¹⁾ Since the temperature dependence in most cases is exactly linear it is in general sufficient to list only a few values. In what follows the refractive index of the extraordinary ray (electric vector parallel to the optical axis) and the index of the ordinary ray (electric vector normal to the optical axis) are designated with n_e and n_o respectively; n_i is the refractive index of isotropic liquid.

The most important results of the measurements can be seen from Fig. 1. This gives the temperature dependence of refractive indices for five homologous thallium soaps ($\lambda = 589$ nm). It is clear that both indices n_e and n_o decrease with the number of C-atoms in the

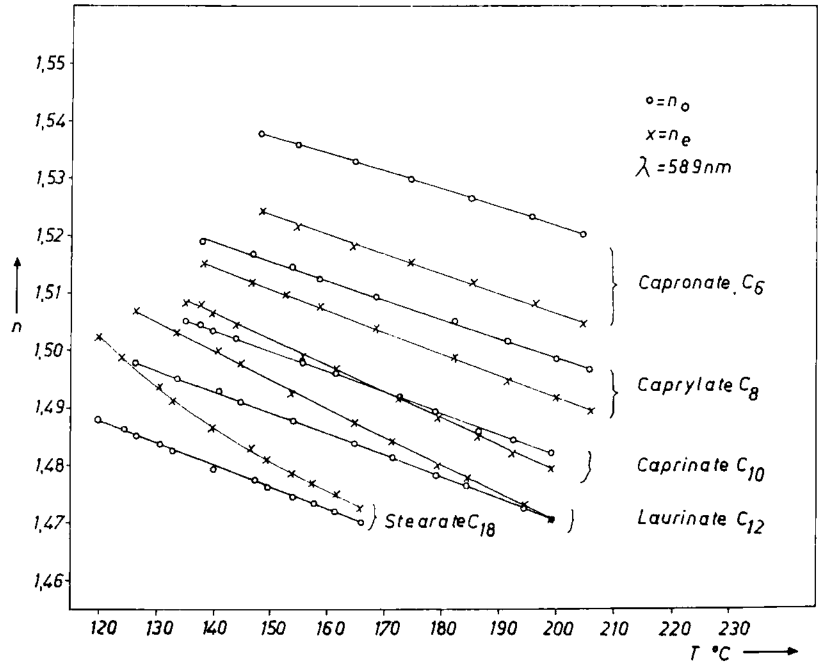

Figure 1. The temperature dependence of double refraction of the neat phase for five homologous thallium soaps (λ = 589 nm).

TABLE 2 Refractive Indices for Thallium Pentanoate

Phase	T °C	436 nm		546 nm		589 nm		644 nm	
		n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
Smectic	207.5	1.5370	1.5670	1.5203	1.5434	1.5165	1.5381	1.5128	1.5333
	195.0	1.5404	1.5708	1.5239	1,5470	1,5203	1.5419	1.5168	1.5367
	180.3	1.5447	1.5751	1.5284	1.5511	1.5247	1.5460	1.5209	1.5408
Plastic modification	176.5	1.5734	1.5764	1.5567	1.5545	1.5523	1.5495	1.5480	1.5445
	125.0	1.5835	1.5844	1.5663	1.5627	1.5621	1.5574	1.5580	1.5524
	85.0	1.5912	1.5908	1.5738	1.5688	1.5698	1.5639	1.5657	1.5588

TABLE 3 Refractive Indices for Thallium Hexanoate

Smectic	204.0	1.5242	1.5466	1.5087	1.5250	1.5047	1.5205	1.5020	1.5161
	175.0	1.5337	1,5560	1.5185	1.5342	1.5150	1.5298	1.5118	1.5248
	148.3	1.5426	1.5649	1.5278	1.5428	1.5241	1.5378	1.5207	1.5330
Plastic modification	144.0	1.5558	1.5600	1.5400	1.5393	1.5370	1.5346	1.5322	1.5300
	139.0	1.5572	1.5602	1.5420	1.5397	1.5384	1.5349	1.5346	1.5302

TABLE 4 Refractive Indices for Thallium Heptanoate

Smectic	207.5	1.5146	1.5323	1.4995	1.5118	1.4961	1.5073	1.4934	1.5029
	170.0	1.5270	1.5436	1.5130	1.5237	1.5097	1.5190	1.5062	1.5145
	144.0	1.5359	1.5519	1.5220	1.5318	1.5188	1.5270	1.5148	1.5224

TABLE 5 Refractive Indices for Thallium Octanoate

Smectic	205.0	1.5070	1.5200	1.4930	1.5012	1.4897	1.4971	1.4862	1.4926
	170.0	1.5205	1.5320	1.5062	1.5128	1.5030	1.5086	1.4998	1.5042
	139.0	1.5321	1.5426	1.5180	1.5231	1.5150	1.5190	1.5117	1.5143

TABLE 6 Refractive Indices for Thallium Nonanoate

Smectic	207.5	1.4964	1.5067	1.4835	1.4900	1.4804	1.4854	1.4772	1.4820
	170.0	1.5130	1.5212	1.5000	1.5034	1.4971	1.4995	1.4938	1.4954
	136.7	1.5274	1.5337	1.5144	1.5154	1.5112	1.5117	1.5080	1.5071

TABLE 7 Refractive Indices for Thallium Decanoate

Smectic	199.0	1.4950	1.5021	1.4825	1.4859	1.4795	1.4823	1.4760	1.4782
	172.5	1.5073	1.5124	1.4946	1.4957	1.4918	1.4920	1.4883	1.4879
	135.0	1.5247	1.5265	1.5120	1.5094	1.5087	1.5052	1.5055	1.5017

TABLE 8 Refractive Indices for Thallium Undecanoate

Smectic	199.0	1.4880	1.4942	1.4763	1.4789	1.4734	1.4751	1.4704	1.4715
	165.0	1.5056	1.5080	1,4930	1.4920	1.4902	1.4880	1.4874	1.4846
	131.0	1.5225	1.5217	1.5098	1.5049	1.5070	1.5011	1.5042	1.4973

TABLE 9 Refractive Indices for Thallium Laurate

Smectic	200.0	1.4850	1.4894	1.4730	1.4738	1.4703	1.4703	1.4676	1.4674
	165.0	1.5023	1.5028	1.4903	1.4872	1.4874	1.4834	1.4845	1.4800
	126.0	1.5223	1.5179	1.5100	1.5016	1.5072	1.4980	1.5041	1.4942

TABLE 10 Refractive Indices for Thallium Myristate

Phase	T °C	436 nm n_i		546 nm n_i		589 nm n_i		644 nm n_i	
Isotr.	197.5	1.4766		1.4638		1.4604		1.4580	
	187.0	1.4810		1.4683		1.4647		1.4619	
		n_e	n_o	n_e	n_o	n_e	n_o	n_e	n_o
Smectic	185.0	1.4827	1.4838	1.4710	1.4700	1.4682	1.4667	1.4652	1.4636
	170.0	1.4902	1.4899	1.4784	1.4755	1.4759	1.4723	1.4730	1.4690
	145.0	1.5042	1.5000	1.4922	1.4851	1.4897	1.4817	1.4868	1.4781
	125.8	1.5150	1.5077	1.5035	1.4926	1.5008	1.4890	1.4980	1.4855

TABLE 11 Refractive Indices for Thallium Palmitate

Phase	T °C	436 nm		546 nm		589 nm		644 nm	
Isotr.	195.5	1.4722		1.4600		1.4569		1.4540	
	178.0	1.4788		1.4667		1.4635		1.4605	
Smectic	176.0	1.4814	1.4809	1.4700	1.4678	1.4674	1.4648	1.4647	1.4617
	165.0	1.4870	1.4852	1.4750	1.4720	1.4728	1.4690	1.4703	1.4654
	145.0	1.4980	1.4932	1.4870	1.4796	1.4841	1.4762	1.4816	1.4728
	120.0	1.5150	1.5030	1.5042	1.4888	1.5015	1.4858	1.4987	1.4824

TABLE 12 Refractive Indices for Thallium Stearate

Phase	T °C	436 nm		546 nm		589 nm		644 nm	
Isotr.	185.0	1.4722		1.4595		1.4565		1.4537	
	166.7	1.4786		1.4660		1.4631		1.4603	
Smectic	166.0	1.4810	1.4701	1.4694	1.4669	1.4667	1.4638	1.4640	1.4610
	150.0	1.4893	1.4861	1.4778	1.4728	1.4754	1.4698	1.4725	1.4667
	135.0	1.4985	1.4920	1.4870	1.4784	1.4848	1.4755	1.4816	1.4723
	120.0	1.5105	1.4979	1.4990	1.4840	1.4960	1.4810	1.4938	1.4778

alkyl chain and with rising temperature. The temperature coefficient of n_e is always larger than that of n_o and is especially clear in the case of the homologues with long chains.

The lower homologues (for instance for $\lambda = 589$ nm the members C_5 to C_9) show negative double refraction ($n_0 > n_e$). This diminishes with decreasing temperature, a phenomenon not observed in the crystalline liquid phases of other substances. With increasing chain length n_o decreases more than n_e. Therefore the negative double refraction diminishes with the chain length. In the middle members of the homologous series (C_{10} to C_{12} for $\lambda = 589$ nm), this behavior causes a point of intersection of the n_e- and n_o-curves at a definite temperature, which varies with the wavelength. Above this temperature the smectic phases exhibit negative double refraction, below this isotropic point positive double refraction. In contrast to the negative double refraction the positive double refraction increases with decreasing temperature. With further lengthening of the chain length the n_o-curve has fully " overtaken " the n_e-curve over the entire range of the liquid crystalline phase. The homologues with longer chains (C_{14}–C_{18}) therefore show only positive double refraction.

The dispersion of double refraction is indicated by the example of thallium undecanoate (Fig. 2). For this substance the neat phase possesses an isotropic point of double refraction at all wavelengths investigated. This shifts with increasing wavelength at higher temperatures. The negative double refraction diminishes with increasing wavelength, the positive double refraction on the other hand increases with wavelength. This is also clear from Fig. 3, which shows the dispersion curves of n_e and n_o at constant temperature ($T_{\text{clearing point}} - 40\,^{\circ}\text{C}$) for three members of the homologous series. It is further clear, that the dispersion of n_e and n_o decreases with increasing chain length.

5. Discussion

The behavior represented by the double refraction of the neat phase of thallium soaps differs from the smectic phases of aromatic compounds.(1,2) For this the structure of the smectic modification of these salts is responsible.

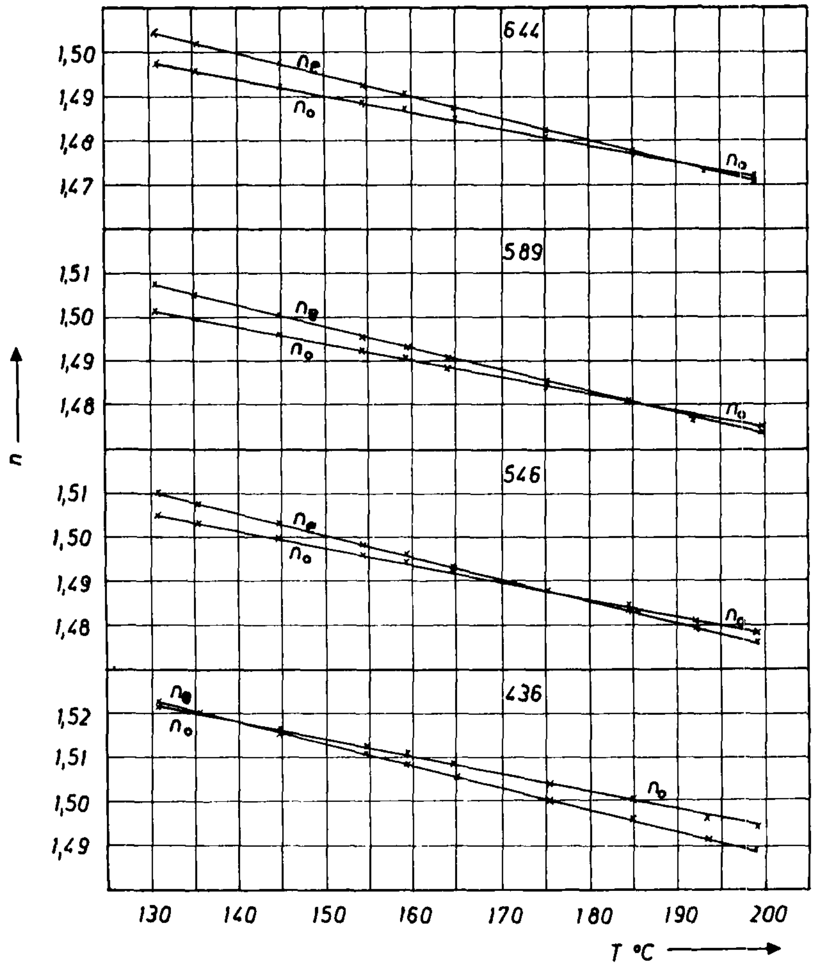

Figure 2. The refractive indices (n_e and n_0) of the neat phase of thallium undecanoate as a function of the temperature for four different wavelengths: 436, 546, 589, 644 nm.

According to Baum *et al.*[3] this structure should be identical with the " structure lamellaire labile " of the neat phases of alkali soaps.[4] In this structure the polar groups of the molecules are arranged in equidistant planes separated by the double layers of paraffin chains (Fig. 4). The alignment of polar groups in the planes is random similar to a two-dimensional liquid. The alkyl chains are not stretched, but more or less bunched together. A shift of layers is

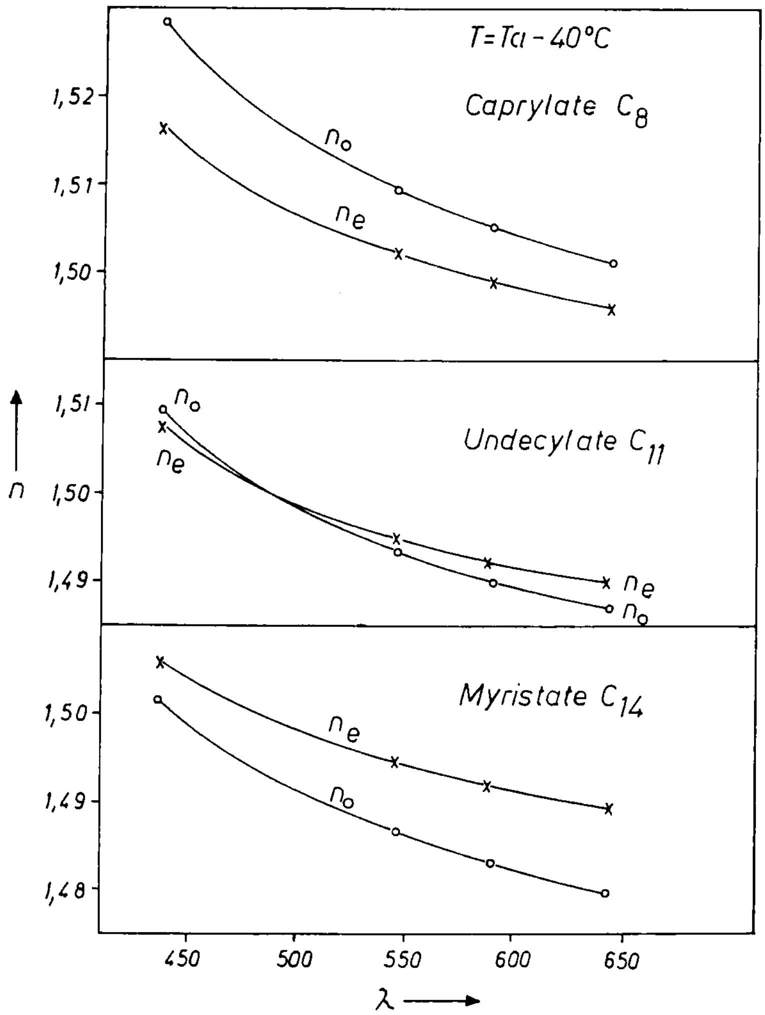

Figure 3. The refractive indices (n_e and n_o) of the neat phase as a function of wavelength and at constant temperature ($T = T_{\text{clearing}} - 40\,°\text{C}$) for thallium octanoate, undecanoate and myristate.

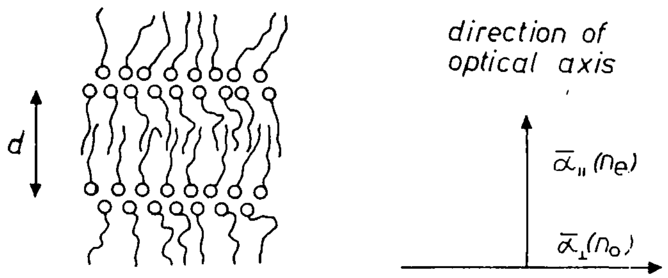

Figure 4. The arrangement of molecules in the " structure lamellaire labile " (schematic).

possible as in the smectic liquids of aromatic compounds. With a rise of temperature the distance of the layers d decreases and the average lateral packing area of each carboxyl group increases. The contraction of chains caused through the temperature mobility of chains is larger the longer the chains.(6) In the homologous series the layer distance and the lateral packing area for each polar group increases with increasing chain length.

In the following discussion we proceed from the Lorenz-Lorentz-formula. According to this the refractive index is dependent on the molar volume V and the polarizability α:

$$\frac{n^2-1}{n^2+2}=\frac{1}{V}\cdot\tfrac{4}{3}\pi\cdot N_L\cdot\alpha$$

n_e is determined by the temporal mean value of polarizability parallel to the optical axis ($\bar{\alpha}_{\parallel}$), n_o by the mean polarizability perpendicular to the optical axis ($\bar{\alpha}_{\perp}$) (Fig. 4). The generally diminution of n_e and n_o with increasing chain length (Fig. 1) is obviously caused by the increase of molar volume with increasing chain length.

Presumably two counteracting specific structural factors determine the polarizability anisotropy $\bar{\alpha}_{\parallel}-\bar{\alpha}_{\perp}$ and consequently the quantity and sign of the double refraction of the orientated crystalline liquid. These are the uniaxial layer arrangement of polar groups and the more or less bunched configuration of hydrocarbon chains between planes. The layer arrangement of the polar groups will give an amount of negative polarizability anisotropy, since the optically uniaxial layer structures usually show negative double refraction.(10)

This amount should diminish with increasing chain length because of the increasing distances between the planes and the increase of the average lateral packing areas of polar groups. The paraffin chains should yield some of positive polarizability anisotropy (respectively, double refraction) because despite bunching, the C—C-bonds should lie generally in the direction normal to the planes (that is the direction of the optical axis) which correspond on the average with a larger longitudinal arrangement of the molecules and a comparatively small cross section.

For the lower homologues the influence of paraffin chains on the sign of double refraction is obviously small and therefore the double refraction is negative. With increasing chain length the influence of positive polarizability anisotropy of paraffin chains increasingly becomes apparent and causes a diminution of negative double refraction with chain length. The competition of the two counteracting influences—the influence of layer arrangement of polar groups and the influence of paraffin chains—can explain the discovered zero position of double refraction in the middle members of the homologous series. For the homologues with longer alkyl chains the amount of positive double refraction of paraffin chains predominates.

On this basis it is possible to explain the different temperature dependence of n_e and n_o. The general decrease of n_e and n_o with increasing temperature is undoubtedly caused by a decrease of density. The increased bunching of the paraffin chains should be responsible for the different temperature coefficients. This implies a decrease of $\bar{\alpha}_{\parallel}$ and an increase of $\bar{\alpha}_{\perp}$. Therefore, n_e increases more with increasing temperature than n_o. The greater temperature coefficients of n_e and n_o in the long chain homologues are convincing because the contraction of chains in consequence of the temperature for long paraffin chains is larger than for short chains.

For those middle members of the homologous series for which the differences between n_e and n_o of the neat phase are very small, the n_e- and n_o-functions intersect because of the different temperature coefficients.

This concept can also be applied to the optical behavior of plastic (possibly likewise liquid crystalline) modifications of thallium-pentanoate (and -hexanoate) which arise by the cooling of the neat

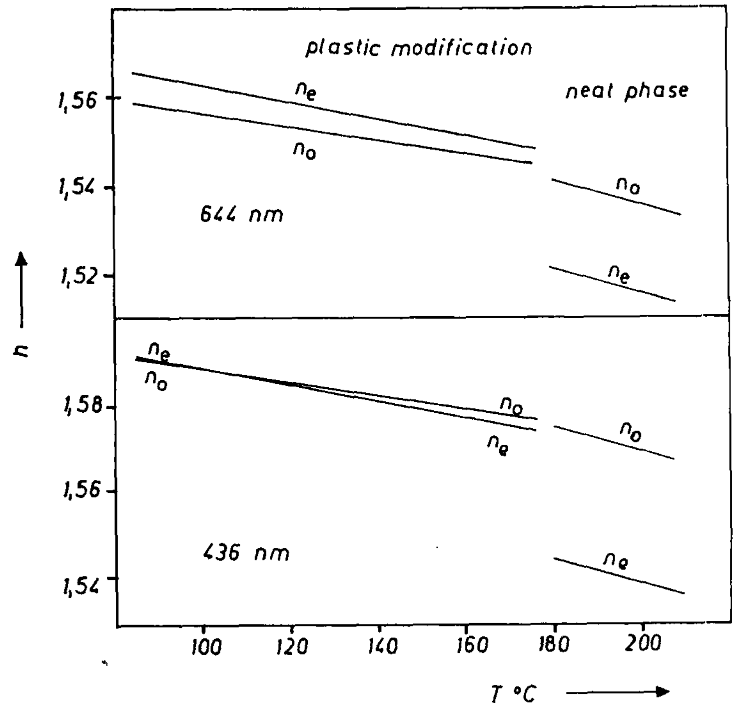

Figure 5. The double refraction of the plastic modification and of the neat phase of thallium pentanoate on dependence of temperature for $\lambda = 436$ nm and $\lambda = 644$ nm.

modification (Fig. 5). The structure of the plastic modification is unknown. We can suppose that, compared with the neat phase, the mobility of the paraffin chains is restricted and the arrangement of polar groups is more compact. The larger stretch of paraffinic chains causes a rise of $\bar{\alpha}_{\parallel}$ as opposed to $\bar{\alpha}_{\perp}$. This could well be the main reason for the fact that compared with the neat phase the n_e-values are much greater. Therefore in longer wavelengths the double refraction becomes positive or is only slightly negative in shorter wavelengths (at higher temperatures).

Moreover the dispersion of double refraction of the plastic modification is similar to that of the neat phase, i.e. with increasing wavelength and decreasing temperature the negative double refraction diminishes and the positive double refraction increases.

This concept about the double refraction of the neat phase of thallium soaps should also be valid for the same modifications of alkali metal soaps. Indeed Oberländer(12) has found in the smectic high temperature modification of three sodium soaps a similar temperature dependence and dispersion of (always slightly positive) double refraction.

For a quantitative discussion, the Lorenz-Lorentz-formula is, of course, not sufficient. For a further separation of the individual influences mentioned, a determination of density-temperature functions is necessary.

An interpretation of the different dispersion of n_e and n_0 and the regular change of dispersion of double refraction with the chain length requires an exact knowledge of UV absorption or UV dichroism of orientated liquid crystalline phases.

Acknowledgement

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