2. The compounds formed by the action of acid chlorides on potassium selenocyanate, although not yet isolated, appear to be very similar in their reactivity to the acyl isothiocyanates and are believed to be acyl isoselenocyanates.

3. Benzoylselenourea possesses a very bitter taste to most individuals, but is tasteless to others, thus emphasizing the similarity of the selenoureas to the thioureas.

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[Contribution from Land-Wheelwright Laboratories]

Optical Properties and Polymorphism of Paraffins

By C. D. West

When a molten paraffin or similar long chain compound is allowed to solidify in a film on a flat glass surface, the film, in spite of being turbid to the naked eye, and showing many randomly oriented small crystals under the microscope, still has sufficient homogeneity to show a peculiar effect when examined with a total reflection refractometer. Instead of one boundary between total and ordinarily reflected light, two such boundaries of a somewhat diffuse character are observed, separated by an interval of up to 0.05 unit in the refractive index scale. The state of polarization of the light at these boundaries proves that the film is optically equivalent to the basal section of a uniaxial positive crystal.

This effect was first described in a paper by Camerer,[1] then by Gaubert,[2] and by Walter.[3] Vorländer and Selke[4] showed that the effect is to be observed with a great variety of pure long chain compounds (paraffins, unsaturated fatty acids, esters of fatty acids, alcohols and ketones, etc.) which solidify in soft solid crystals.

In the past year Page[5] published measurements on five natural paraffins with melting points in the range 49.4–60.6°. Page assigned an incorrect optical character to his films; he arbitrarily called the ordinary refractive index the extraordinary, and *vice versa*. His calculations based on this error are accordingly incorrect. He carried his measurements for each specimen through a considerable temperature range. The irregularity of these curves at temperatures near the melting points suggests that at least some of his materials (for example, that melting at 60.6°) underwent polymorphic transitions in the course of the measurements, as they would be expected to do according to the X-ray structure work that has been published on this point.

More recently Seyer and Fordyce[6] gave refractive index data for the pure paraffin dicetyl (dotriacontane, $C_{32}H_{66}$) in the solid state from 30° up to the melting point, 70°. These writers failed to note the double edge of total reflection, nor did they take into consideration the fact that this material has a sharp reversible inversion at 5° below its melting point. Rather they concluded from their refractive index curve, together with the solubility curves in propane and butane, that dicetyl has a transition at 55°.

The prior work of Piper and co-workers[7] showed clearly that dicetyl has a sharp reversible transition at about 65°. This was observed macroscopically, microscopically and by means of X-rays. Other straight chain paraffins near to dicetyl all exhibit the same transition about 5° below the melting point.[8]

In the following is described a repetition of the work of Seyer and Fordyce with dicetyl, rather for the purpose of illustration than to give the precise numerical constants of this material in a state of known purity.

Experimental

An Abbe refractometer with front opening for the front or refracting prism (Bausch and Lomb) was used. The dicetyl was obtained from Eastman Kodak Company; it melts sharply at 69.5–69.7°, and solidifies at 68.8–67.7°. For some of the measurements the molten material was poured onto the refracting prism and allowed to solidify without closing the back prism; for others the back prism was closed after melting the material on the front prism. The character and position of the edges is the same in the

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(1) R. Camerer, *Ann. Physik*, **54**, 84–103 (1895).

(2) P. Gaubert, *Bull. soc. franç. minéral.*, **33**, 326 (1910).

(3) R. Walter, *Ber.*, **59**, 971–972 (1926).

(4) D. Vorländer and W. Selke, *Z. physik. Chem.*, **129**, 435–474 (1927).

(5) J. M. Page, Jr., *Ind. Eng. Chem.*, **28**, 856–859 (1936).

(6) W. F. Seyer and R. Fordyce, This Journal, **58**, 2029 (1936).

(7) S. H. Piper and others, *Biochem. J.*, **25**, 2027 (1931).

(8) L. Deffet, *Bull. soc. chim. Belg.*, **44**, 97 (1935), reported the melting point 70.0° and the transition point 64.3° for dicetyl at atmospheric pressure.

two cases, but of course the temperature control is better when the prisms are closed and water circulates about both of them.

The character of the edges was identified with a polarizing disk (obtainable from the Polaroid Corporation, Boston, or other dealers) over the ocular. The well-known rule for uniaxial sections or films perpendicular to the optic axis may be stated: When the vibration direction of the polarizer is vertical, *i. e.*, parallel to the plane of incidence, the boundary marking the ordinary index disappears, the sharpness of the extraordinary boundary is enhanced; when the vibration direction of the polarizer is horizontal, *i. e.*, perpendicular to the plane of incidence, the extraordinary boundary disappears, the sharpness of the ordinary boundary is enhanced. If the film under examination is isotropic, the boundary marking its refractive index does not disappear for any azimuth of the polarizer. These statements are true, whether the light is admitted through the front prism (reflection position) or through the back prism (grazing incidence position). A polarizer is indispensable in work with materials that may form anisotropic films, in *finding*, in *identifying*, and in *setting on the cross hairs* the boundaries observed with a total reflection refractometer.

Other materials known to form, under suitable conditions, uniaxial films on flat glass surfaces are liquid crystalline substances, cellulose derivatives, gelatine, agar, etc. I hope to describe some of these films at a later date.

Results

Refractive index measurements of dicetyl, believed to be accurate to better than 0.001 unit, are shown in Table I and by the smoothed curve of Fig. 1. For the transition temperature Piper's mean value of 64.6° is assumed to be correct. On cooling through this temperature a marked change in the appearance of the film between the Abbe prisms is noted (the same changes are seen in a film formed on a slide under a cover glass): the texture changes from fine-grained to coarse-grained, and air bubbles appear, probably because of the contraction in volume. At the transition temperature both refractive indices change by 0.018 unit.

TABLE I

REFRACTIVE INDICES OF DICETYL IN THE LIQUID AND TWO SOLID PHASES

Temp., °C.	ε		ω
20	1.5645		1.5148
30	1.5625		1.5126
40	1.5593		1.5096
50	1.5553		1.5053
60	1.5500		1.5000
64.6	1.5472		1.4971
64.6	1.5290		1.4788
67.5	1.5270		1.4768
69.6	1.5257		1.4756
69.6		1.4358	
75		1.4338	
80		1.4325	

It will be noted that the birefringence of a solid dicetyl film is the same, about 0.050, in its two phases, and does not vary sensibly with temperature. It might have been expected to be higher for the high temperature form, for Piper and his co-workers found the molecular axes to be perpendicular to the basal plane in the high temperature or A-form (d_{001} 42.33 Å.), but to have some obliquity thereto in the low temperature or C-form (d_{001} 37.8 Å.).

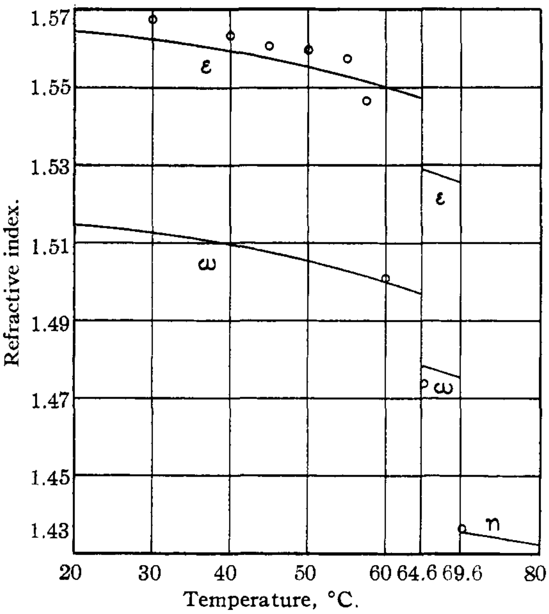

Fig. 1.—Refractive indices of dicetyl in the liquid and two solid phases.

The circles in Fig. 1 represent the measurements of Seyer and Fordyce. It is seen that while their points agree with the interpretation that dicetyl has a transition about 5° below the melting point, their conclusion that a transition occurs at 55° is forced and erroneous.

Summary

The simple procedure is described for measuring, by means of a total reflection refractometer equipped with a cap polarizer, the refractive indices of materials which solidify to form transparent uniaxial films. The dimorphism of solid dicetyl is demonstrated by refractometric measurements, and approximate values of its optical constants are given over a range of temperatures.

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