CHAPTER II

STUDIES ON BIREFRINGENCE AND ORDER PARAMETERS IN SOME LIQUID CRYSTALS.

Introduction:-

Birefringence is an important and interesting property of liquid crystals. A convenient way to identify a liquid crystalline material is to test it for birefringence. Microscopic observation of nematic liquid crystals between crossed polarisers show that it behaves optically like uniaxial crystals and exhibits positive birefringence. Birefringence arises due to the alignment of molecules with large molecular anisotropy. In liquid crystalline phase the optical birefringence increases with increasing molecular alignment. It can therefore be used as a measure of the ordering of the molecules. As the temperature of the nematic liquid crystal is increased the birefringence $\Delta n = n_e - n_o$ decreases. Where ne is the extraordinary refractive index and no the ordinary refractive index. At the transition temperature T_{NI} from nematic to isotropic phase a step like change of both the coefficient takes place and they reach a value n_{iso} which is the characteristic of isotropic liquid. Consequently the value of birefringence falls step wise to zero.

The liquid crystalline phase being more ordered than the high temperature isotropic liquid, an 'order parameter' is defined such that it is nonzero in the nematic phase and vanishes due to the symmetry reasons in the isotropic phase. Because of the thermal motion, the molecules in a nematic liquid are not all exactly parallel but the extent of parallelism can be measured by the order parameter.

On microscopic approach, where the molecules are supposed to be simple rod like, the measure of the alignment along the director $\hat{n}$ is given by

$$S = 1/2 \langle (3 \cos^2\theta - 1) \rangle \text{ ------- } (1)$$

Where θ is the angle between the long axis of a molecule and the axis of preferred orientation which coincides with the symmetry axis in uniformly oriented nematic liquids.[1-3]

For perfect parallel orientation of the molecules S = 1 and for the isotropic liquid S = Ø.

The macroscopic defination of the order is independent of the assumption on molecular rigidity.

Any of the bulk tensorial property such as refractive index, dielectric constant, magnetic susceptibility etc can be used to determine the order parameter.

The tensor order parameter is given by

$$Q_{\alpha\beta} = G\left(\epsilon_{\alpha\beta} - \frac{1}{3}\delta_{\alpha\beta}\epsilon_{\gamma\gamma}\right) \cdots\cdots (2)$$

$\epsilon_{\alpha\beta}$ may be taken as the electric polarizability, dielectric constant or magnetic susceptibility, G is the normalization constant.

A simplified connection between the macroscopic tensors and the microscopic quantities can be obtained by assuming the molecules to be approximately rigid. Considering the molecules to be uniaxial rods, Saupe[4,8] found the relation

$$S = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \cdots\cdots\cdots (3)$$

α_e and α_o are the principal polarizability of the mesomorphic phase $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the longitiduinal and transverse component of the perfect molecular polarizability tensor.

Becauase of the effects of the local fields on various tensorial properties the macroscopic order parameter Q which is determined using these properties differ among themselves and also from the microscopic order parameters. Assuming the validity of a given local field model, it is possible to determine the microscopic order parameters from the knowledge of the macroscopic tensorial properties.[1,5-7]

A knowledge of polarization field is required for the determination of the order parameters in nematic liquid crystals from the optical anisotropy. The problem of the local electric field has been treated mainly from two different approaches. viz i) the use of Vuk's formula[8] which assume an isotropic local field, and ii) the use of Neugebauer's relation[9,10] obtained from the point dipole approximation and involving an anisotropic local field. A third approach has been used by Deizhanski and Petrov[11] and by Jeu and Bordewijk.[12] In their model it is assumed that the molecules occupy a spheroidal cavity whose volume is equal to the volume available to the molecule and that the spheroial sphaped molucule is uniformly polarizable and the medium surrounding the spheroidal cavity is a homogeneous anisotropic dielectric. Actually the molecules are of finite size and have irregular shapes and consists of groups which are polarizable to different extents. Further immediate vicinity of a molecule cannot be approximated by a continuous medium. Therefore, the calculations from the cavity field determined by the electrostatic theory with the application, of the boundary condition, for a spheroidal cavity, are not likely to lead to the true value. However, it is found that the orientational order parameters evaluated through the different approaches mentioned above are reasonably consistent with the values obtained from other studies such as diamagnetic anisotropy, NMR etc. Madhusudana[13] has drawn some theoritical conclusions about the reliability of the density and refractive index measurement used for evaluating the order parameter.

The orientational order parameter S of a liquid crystal is an important parameter, the knowledge of which is essential for use in a specific purpose. Various methods are now being used to measure the order parameter as has been discussed by Saupe and Maier namely nuclear magnetic resonance, dielectric permittivity diamagnetic susceptibility, refractive indices, x-ray scattering, UV and IR dichroism etc. The author has made an extensive investigation on the order parameter of some liquid crystals from the measurements of refractive indices and densities at different temperatures in the nematic and isotropic phases.

The object of the present studies were to find the order parameter of various liquid crystal samples by the methods of Vuk's isotropic internal field and Neugebauer's anisotropic field and to compare them. Also to find the change in the order parameter for the biphenyl liquid crystals, when a phenyl ring is substituted by cyclohexyl ring.

Various researchers has shown considerable interest in studying the temperature dependence of refractive indices by prism refractometer method.[14,15] Recently the laser light has been used for the determination of birefringence.[16,17]

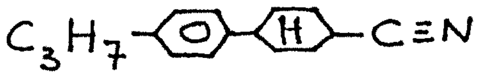
Yalhmi et al[18] have studied the refractive indices in the nematic and isotropic phases of P - n - butoxy and P - n amyloxy benzoic acids. The higher values of the order parameter by using Vuk's formula are attributed to the dimer formation and to the existence of a dimer - monomer equilibrium. Sarna et al[19] have studied the polymesomorphic HBT and OBT using wedge method for the determination of the refractive indices and found that the order parameter values determined using Vuk's and Neugebauer's models agree in the nematic phase but differ in the smectic phase.

The refractive indices in oriented cholesteryl dodecyl carbonate and a smectic liquid crystal P - n-octyloxy benzylidene P - n-butylanilin have been measured as a function of temperature and the order parameter reported.[20] The voltage and wavelength dependence of refactive indices have been measured by the interferogram technique.[21] Shashidhara[22] and co-workers have reported the refractive indices in nematic, re-entrant isotropic and isotropic phases. Rao et al[23] with the refractive index data, have computed the molecular polarizabilities and its anisotropies at different wavelengths by using different internal fields. Chandrasekhar et al[24] developed a theory of the birefringence of[25] nematic liquid crystals. Recently Sen[25] and co-workers have evaluated the birefringence and order parameter of some alkyl and alkoxy cyanobiphenyl liquid crystals. They have calculated the effective polarizabilities α_e and α_o in the nematic phase using the methods of Neugebauer's, Vuk's and Saupe and Maier. Although the values of the effective polarizabilities are found to be appreciably different the order parameter S, evaluated with those values of $(\alpha_e - \alpha_o)$ are in good agreement. Hauser[26] has found that the birefringence and refractive index alternate with carbon number of the alkyl chains in a homologous series of nematics. Refractive indices, densities, and optical anisotropy of Cholesteric liquid crystals has been studied by Somashekhar[27] and Shivprakash[28]. They found a decrease in effective optical anisotropy with increase in temperature resulting in the decrease in orientational order.

EXPERIMENTAL:

The structural formulae and nematic - isotropic transition temperatures in degree celcius of the studied liquid crystals are given below:

1. p-cyano - p' - propylphenylcyclohexane (PCH-3)



$$C \xrightarrow{43^{\circ}} N \xrightarrow{45^{\circ}} I$$

2. p-cyano - p' - pentylphenylcyclohexane (PCH-5)

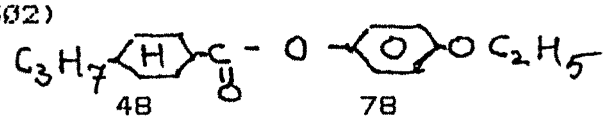
$$C \xrightarrow{30} N \xrightarrow{55} I$$

3. p-cyano - p' - heptylphenylcyclohexane (PCH-7)

$$C \xrightarrow{30} N \xrightarrow{57} I$$

4. Ethoxyphenyl - trans - 4' - propylcyclohexylcarboxylate

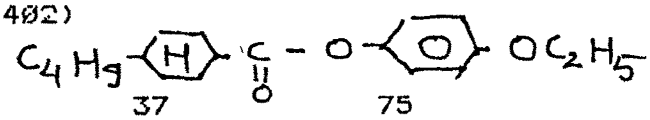
D-(302)



$$C \xrightarrow{48} N \xrightarrow{78} I$$

5. Ethoxyphenyl - trans - 4' - butylcyclohexylcarloxylate

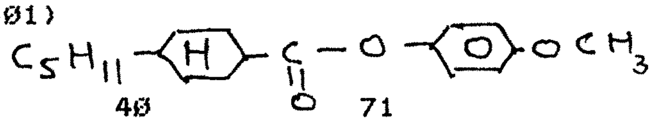
D-(402)



$$C \xrightarrow{37} N \xrightarrow{75} I$$

6. 4-methoxyphenyl - trans - 4' - pentylcyclohexylcarloxylate

D-(5Ø1)

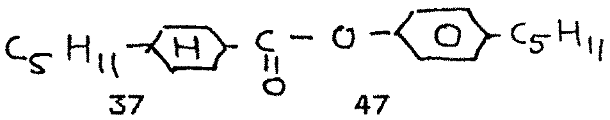


40 71

C ----> N -----> I

7. 4-Pentylphenyl - trans - 4' -pentylcyclohexylcarloxylate

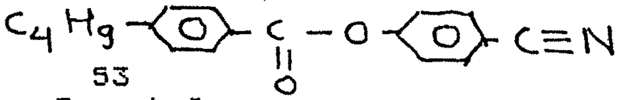
D-55



37 47

C ----> N -----> I

8. p-cyanophenyl - p' - butylbenzoate (CPBB)

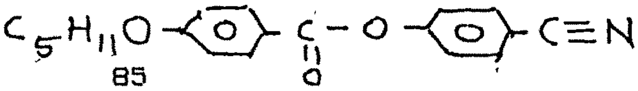


53

C----> I

N 43

9. p-cyanophenyl - p' - pentyloxybenzoate (CPPOB)

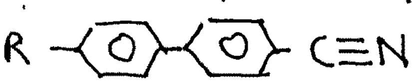


85

C----> I

N 76.5

1Ø Mixture E-4 composed of cyano biphenyles.



4 61

C----> N ----> I

Heptylcyanobiphenyl (7CB), Pentyloxycyanobiphenyl (5OCB), Heptyloxycyanobiphenyl (7-OCB), octyloxy cyanobiphenyl (8-OCB), in the proportion of 44:19:16:21.

11 Mixture E-7 composed of (5CB), (7CB), (8-OCB) and (T15) (pentylphenylcyanobiphenyl) in the proportion of 47:25:18:10

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    10        58
C----> N ----> I
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12 Trans trans - 4' - propylbicyclohexyl - 4 - carboxynitril (propylcyclohexylcyclohenxane) (CCH- 3).

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    46        49
C----> N ----> I
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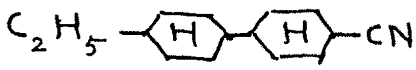
13 Trans trans - 4' - ethylbicyclohexyl - 4 - carboxynitril (ethylcyclohexylcyclohenxane) (CCH- 2).



T_{CN} = 58 T_{NI} = 80 T_{SN} = 57

14 Trans trans - 4' - pentylbicyclohexyl - 4 - carboxynitril (pentylcyclohexylcyclohenxane) (CCH- 5).

T_{CN} = 62 T_{NI} = 85.2 T_{SN} = 52

15 Trans trans - 4' - heptylbicyclohexyl - 4 - carboxynitril (heptylcyclohexylcyclohenxane) (CCH- 7).

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    71        82.1
C----> N ----> I
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The transition temperatures were noted with the help of a hot stage polarising microscope. The liquid crystals were obtained from BDH, Eastman Kodak. England and E.Merck, and were used in the investigations without further purification.

Measurement of refractive indices:-

The refractive indices of the extraordinary ray ne and ordinary ray no in the nematic phase and refractive index n in the isotropic phase at different temperatures were measured by means of an Abbe refractometer. All the measurements were carried out while cooling the sample.

The schematic view of the divergent opitcal paths through the refractometer which result when light is incident perpendiculer to the optic axis of the mesophase is shown in the fig.2.

The glass prisms of the refractometer were dried. The Prism was then first treated with an aqueous solution of 3% polyvinyl alcohol and rubbed with a lens paper along the length of the prism several times. A little of the liquid crystal was dropped on the lower prism and was spread with a spatula. These operations helped to align the molecules of the liquid crystals along the prism face. The alignment was complete when the upper prism was clamped in place.

The two positions of a nicol placed over the eyepiece allows distinct separation of the dark and bright space in the eyepiece corresponding to n_e and n_o (in the nematic $n_e > n_o$). A second nicol placed between the light source and lower prism makes the separation between the dark and bright space sharper. The temperature of the refractometer was maintained constant within ± 0.2 degree C by means of a thermostat. Where the value of the

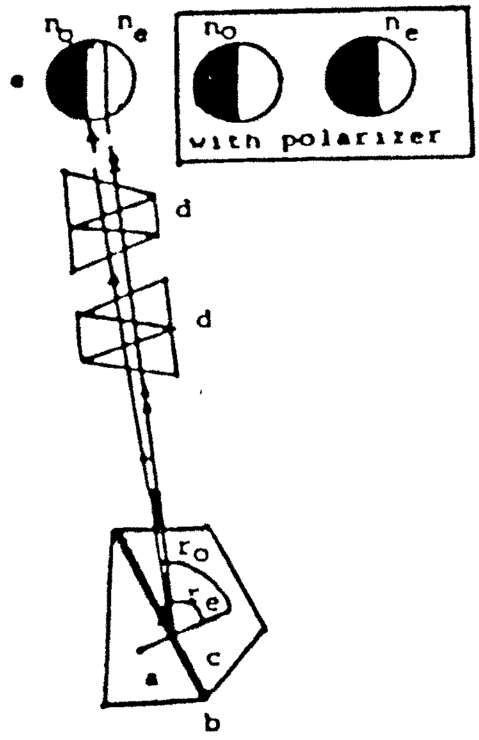


Figure 2. Schematic of the refraction by a birefringent material in a Abbe refractometer.

a = is the illuminating prism

b = is the mesophase,

c = is the refracting prism,

d = is an Amici prism,

e = is the field viewed through the ocular of the refractometer,

re = is the angle of refraction associated with extraordinary ray.

ro = is the angle of refraction associated with the ordinary ray.

refractive index ne for extraordinary ray lay outside the range of the refractometer ($n_e > 1.70$) it was calculated from the relation $n = 1/3\ (2 n_o + n_e)$ when n is the isotropic refractive index extrapolated at the appropriate temperature.

Measurement of Densities.:-

The densities of the liquid crystals in the nematic and isotropic phases were determined with the help of a picnometer. Weighed sample of the liquid crystal was introduced through the capillary tube into the bulb placed in a thermostat. The length of the column in the capillary was measured at different temperatures with a travelling microscope. The density was calculated after correcting for the expansion of the glass tube.

Results and Discussions.:-

The results of the refractive indices of the liquid crystals studied in the isotropic phase n and in the nematic phase ne and no (extrodinary and ordinary refractive indices) together with the densities of the liquid crystals at different temperatures are given in Tables 2.1 (a-o) .

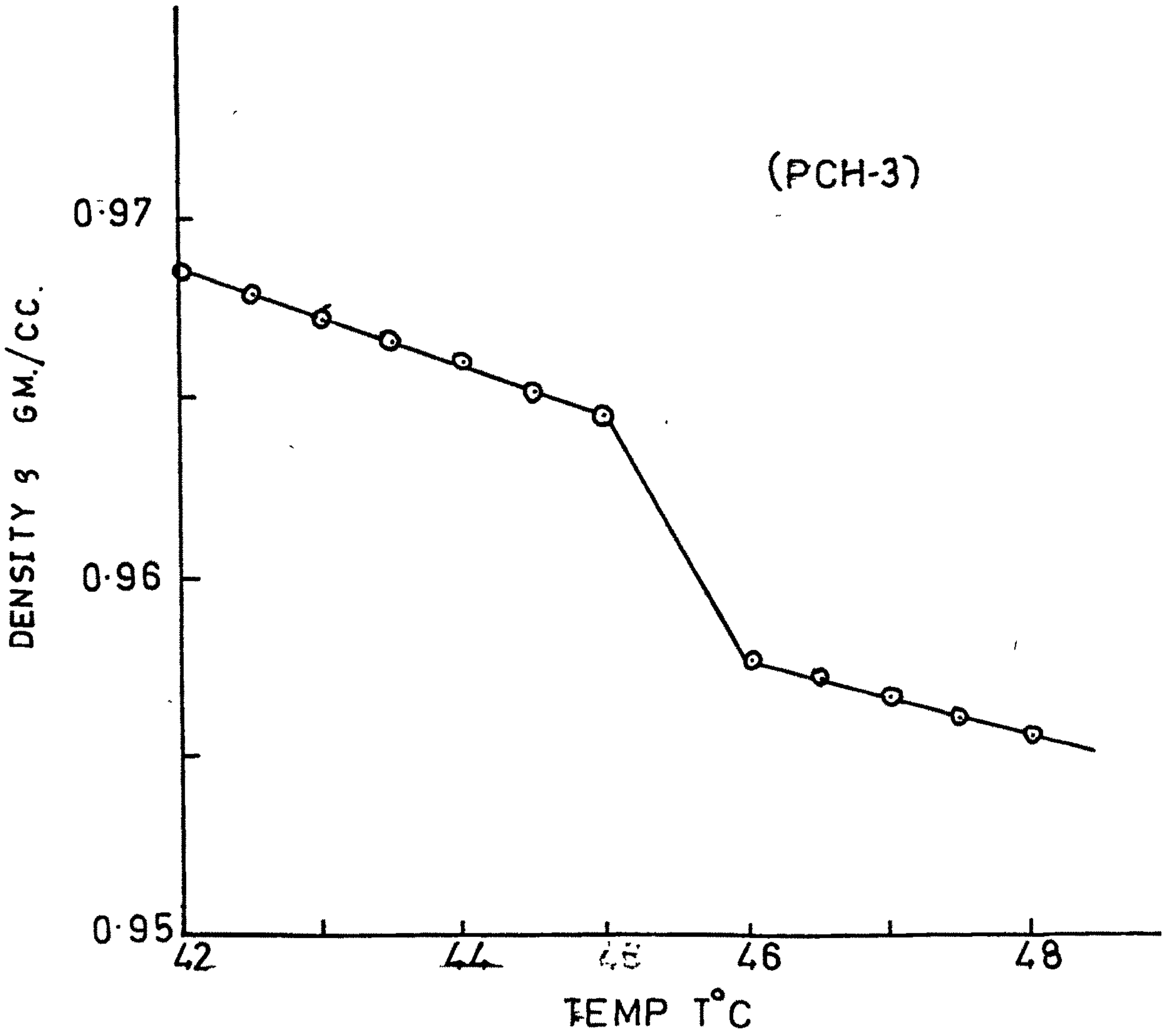
Temperature variation of densities in the liquid crystals.

Figure 2.1 a (i) to 2.1 o (i) represents the temperature variation of the densities in the different liquid crystals studied. It can be seen from the figures that the density shows a linear variation in both the nematic and isotropic phases away from the transition. A sudden jump in the value is found in the range of about 2 degree C near the isotropic - nematic phase

Table 2.1 (a)

Temperature variation of density (ρ) and refractive indices n_o , n_e and n_{iso} of PCH-3

Temp degree C	ρ gm/cc	no	ne
42	0.9685	1.4912	1.5852
42.5	0.9678	1.4913	1.5842
43	0.9672	1.4920	1.5820
43.5	0.9666	1.4920	1.5814
44	0.9660	1.4928	1.5787
44.5	0.9652	1.4930	1.5775
45	0.9645	1.4936	1.5755
46.	0.9576	1.5208	
46.5	0.9571	1.5205	
47	0.9567	1.5201	
47.5	0.9560	1.5200	
48	0.9555	1.5197	


(PCH-3)
DENSITY ϱ GM./CC.
0·97
0·96
0·95
42
44
46
48
TEMP T°C

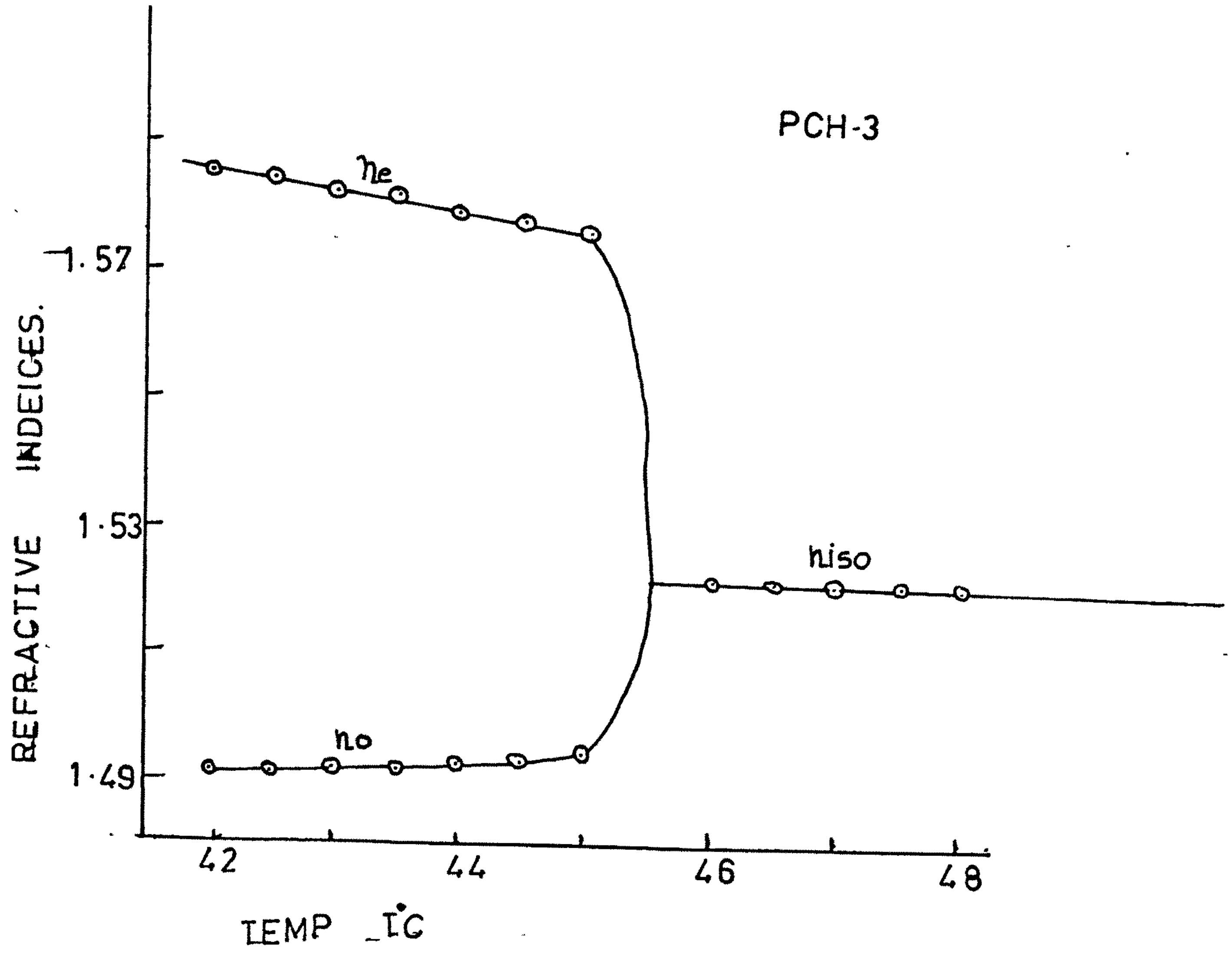

PCH-3
ne
no
niso
1.57
1.53
1.49
REFRACTIVE INDEICES.
42
44
46
48
TEMP _ °C

Fig. 2.1 a(ii)

Table 2.1 (b)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of PCH-5

Temp degree C	ρ gm/cc	n_o	n_e
31	0.9610	1.4870	1.6000
33	0.9593	1.4864	1.5979
35	0.9582	1.4860	1.5953
37	0.9565	1.4860	1.5918
39	0.9548	1.4860	1.5880
41	0.9529	1.4860	1.5849
43	0.9512	1.4860	1.5783
45	0.9492	1.4860	1.5746
47	0.9473	1.4860	1.5711
49	0.9451	1.4860	1.5654
51	0.9423	1.4870	1.5554
54	0.9389	1.4898	
56	0.9336	1.5105	
58	0.9317	1.5095	
60	0.9300	1.5081	
63	0.9273	1.5075	

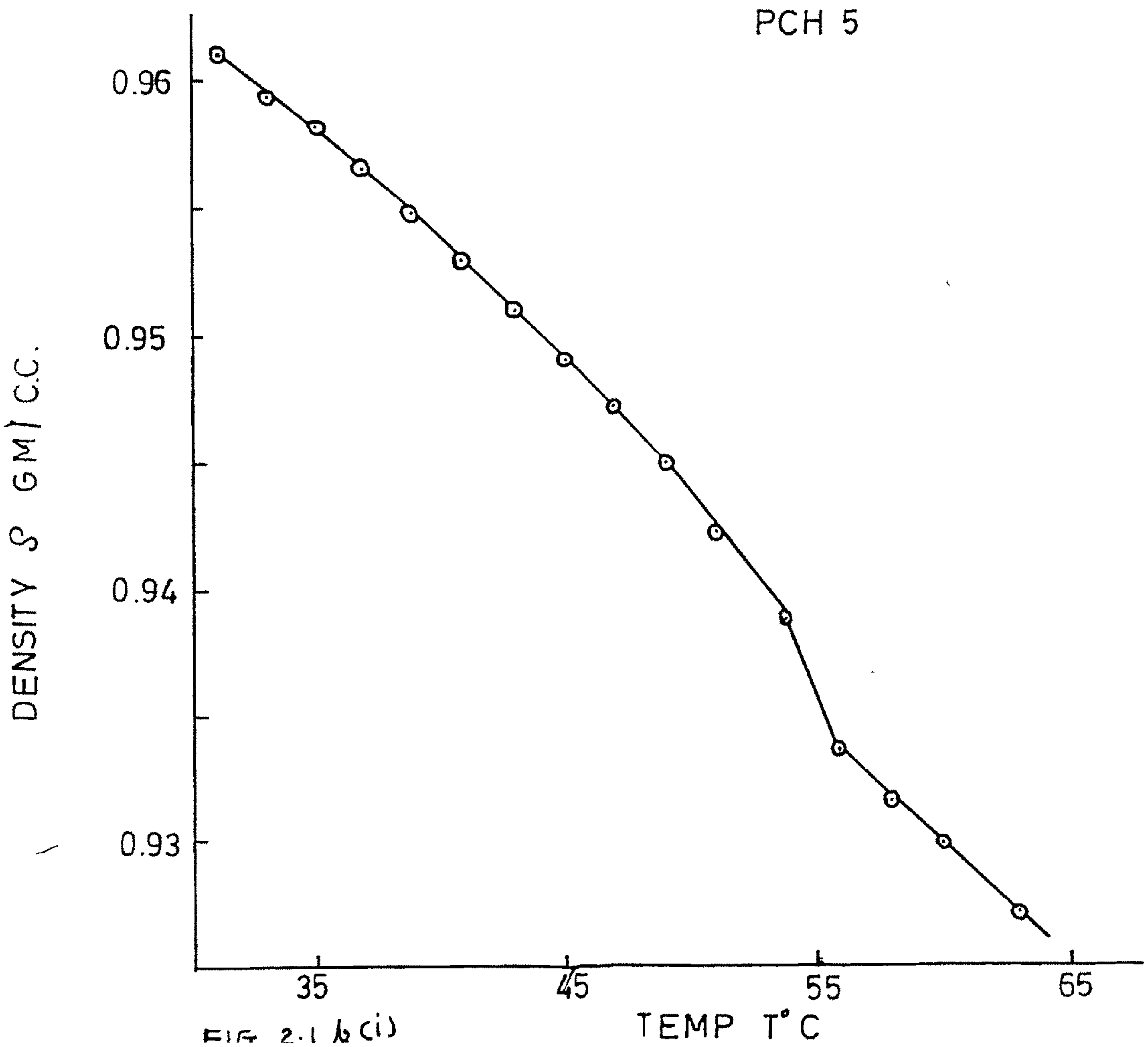
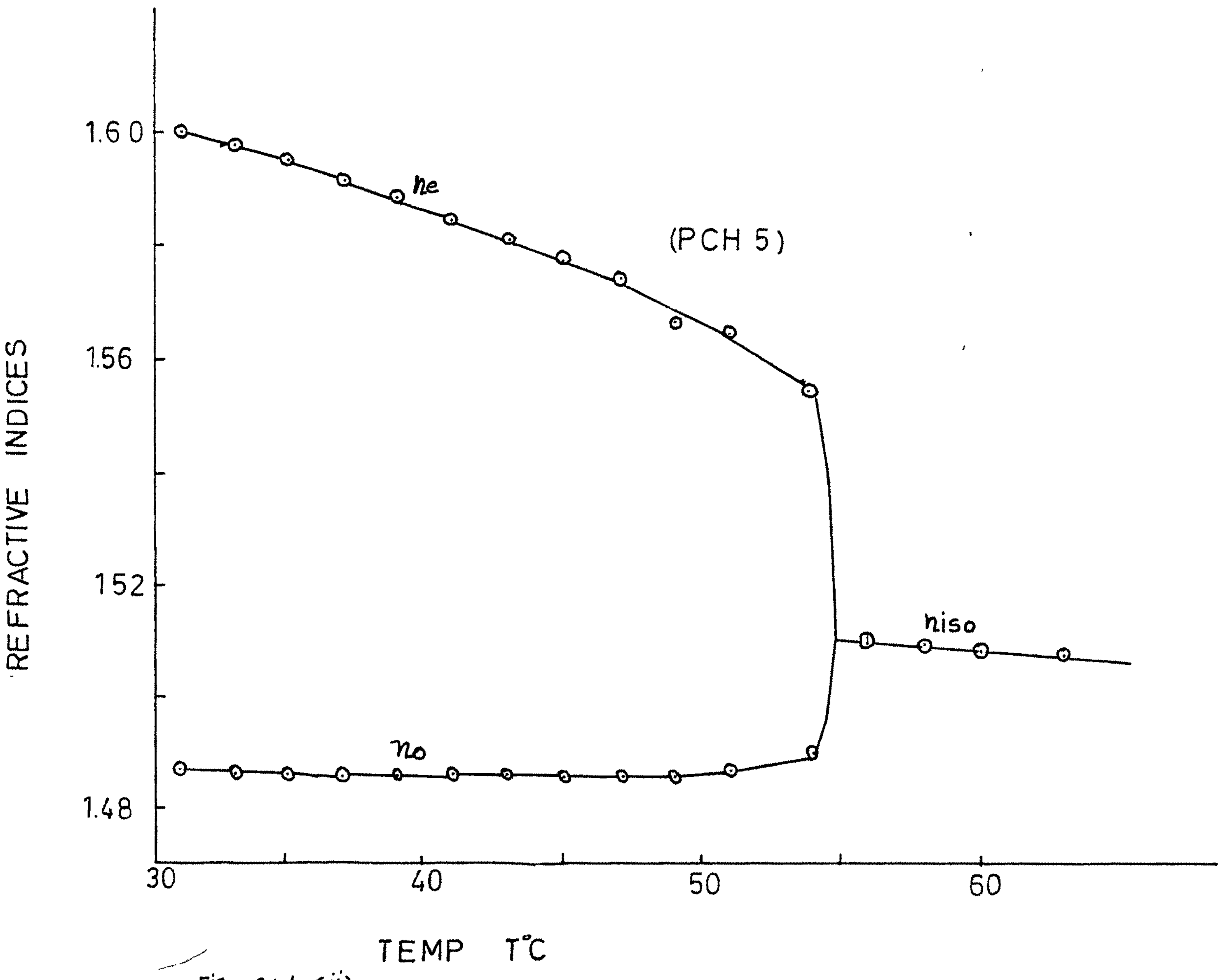


FIG 2.1 b(i)



REFRACTIVE INDICES
1.60
1.56
152
1.48
ne
no
niso
(PCH 5)
30
40
50
60
TEMP T°C

Fig. 2.1 b (ii).

Table 2.1 (c)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of PCH-7

Temp degree C	ρ gm/cc	no	ne
31	0.9499	1.4840	1.5964
33	0.9489	1.4838	1.5934
35	0.9467	1.4836	1.5903
37	0.9445	1.4832	1.5867
38	0.9429	1.4830	1.5842
39	0.9411	1.4825	1.5814
41	0.9394	1.4822	1.5783
43	0.9375	1.4820	1.5752
45	0.9355	1.4820	1.5720
47	0.9335	1.4822	1.5679
49	0.9316	1.4830	1.5645
51	0.9293	1.4842	1.5598
53	0.9268	1.5055	1.5559
55	0.9205	1.5040	1.5498
58	0.9165	1.5035	
59	0.9160		
61	0.9145		

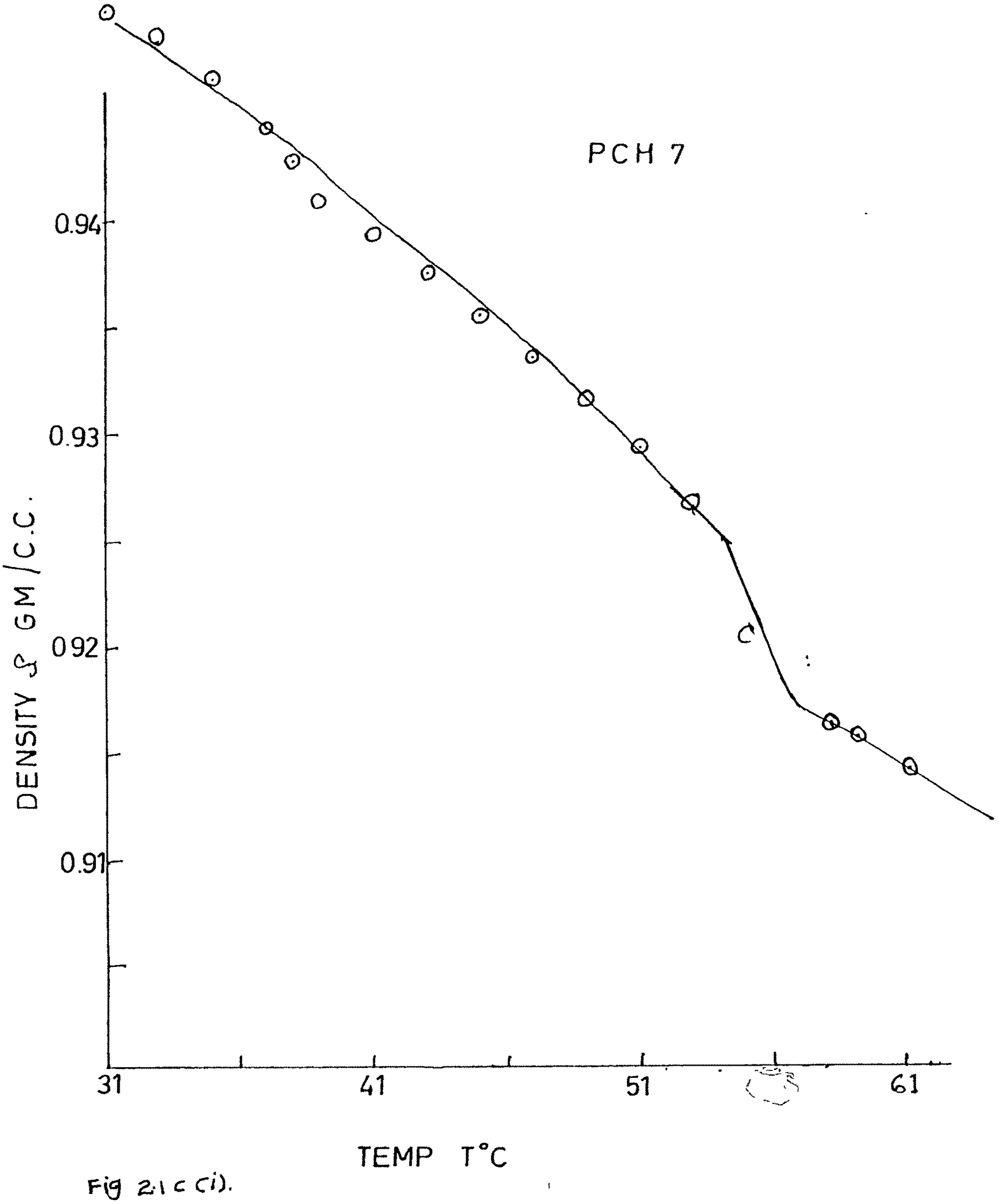


Fig 2.1 c (i).

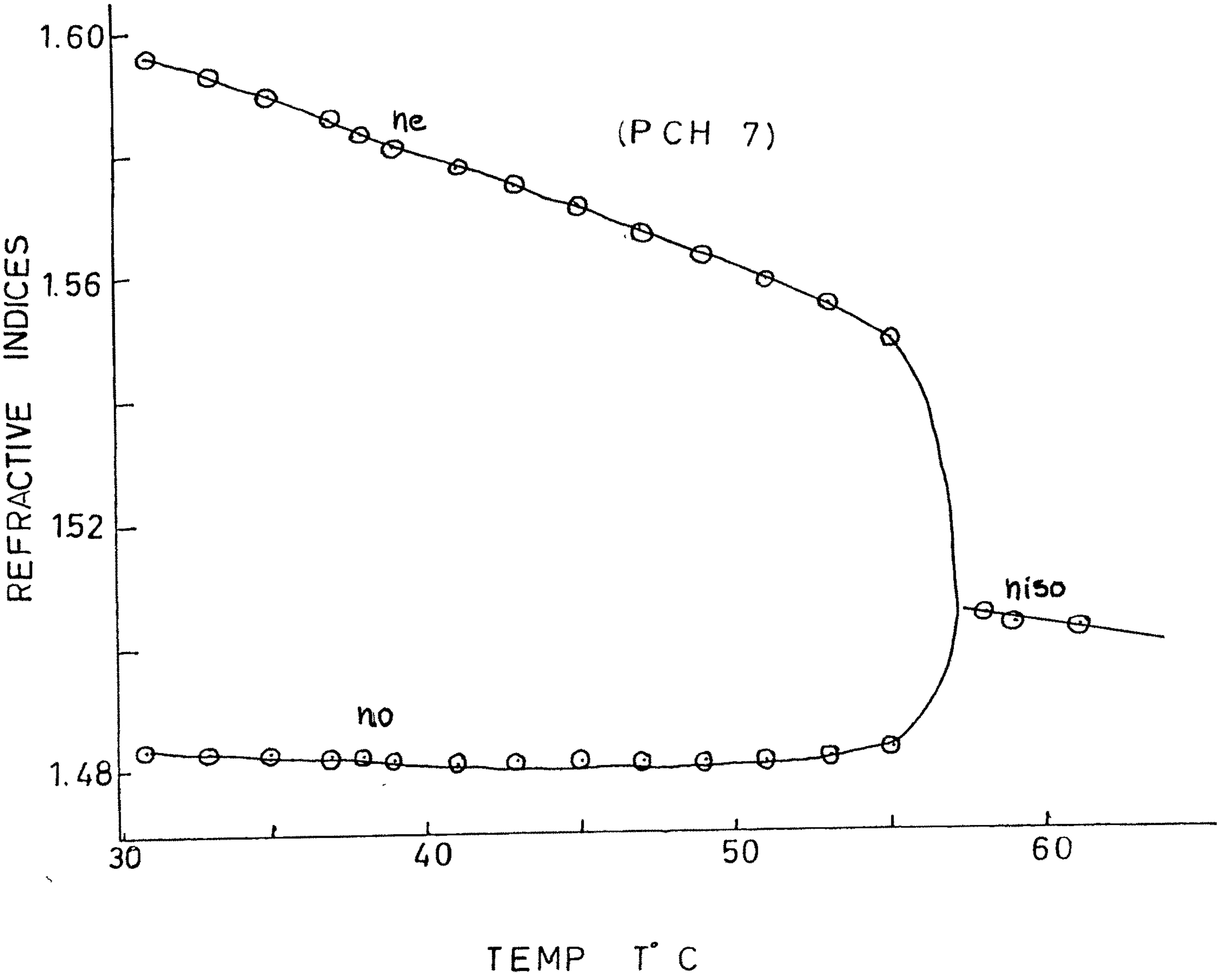

REFRACTIVE INDICES
1.60
1.56
152
1.48
ne
(PCH 7)
niso
no
30
40
50
60
TEMP T° C

Fig 2.1C(ii)

Table 2.1 (d)

Temperature variation of density (ρ) and refractive indices n_o , n_e and n_{iso} of D - 302.

Temp degree C	ρ gm/cc	no	ne
51	1.0118	1.4705	1.5448
54.5	1.0093	1.4700	1.5417
57	1.0074	1.4693	1.5401
60	1.0048	1.4684	1.5384
63	1.0024	1.4680	1.5356
66	1.0000	1.4677	1.5327
69	0.9974	1.4677	1.5289
72	0.9947	1.4674	1.5263
75	0.9921	1.4677	1.5222
77	0.9900	1.4680	1.5198
78	0.9888	1.4698	1.5146
79	0.9849	1.4845	
80	0.9841	1.4842	
84.5	0.9804	1.4824	
88	0.9776	1.4810	

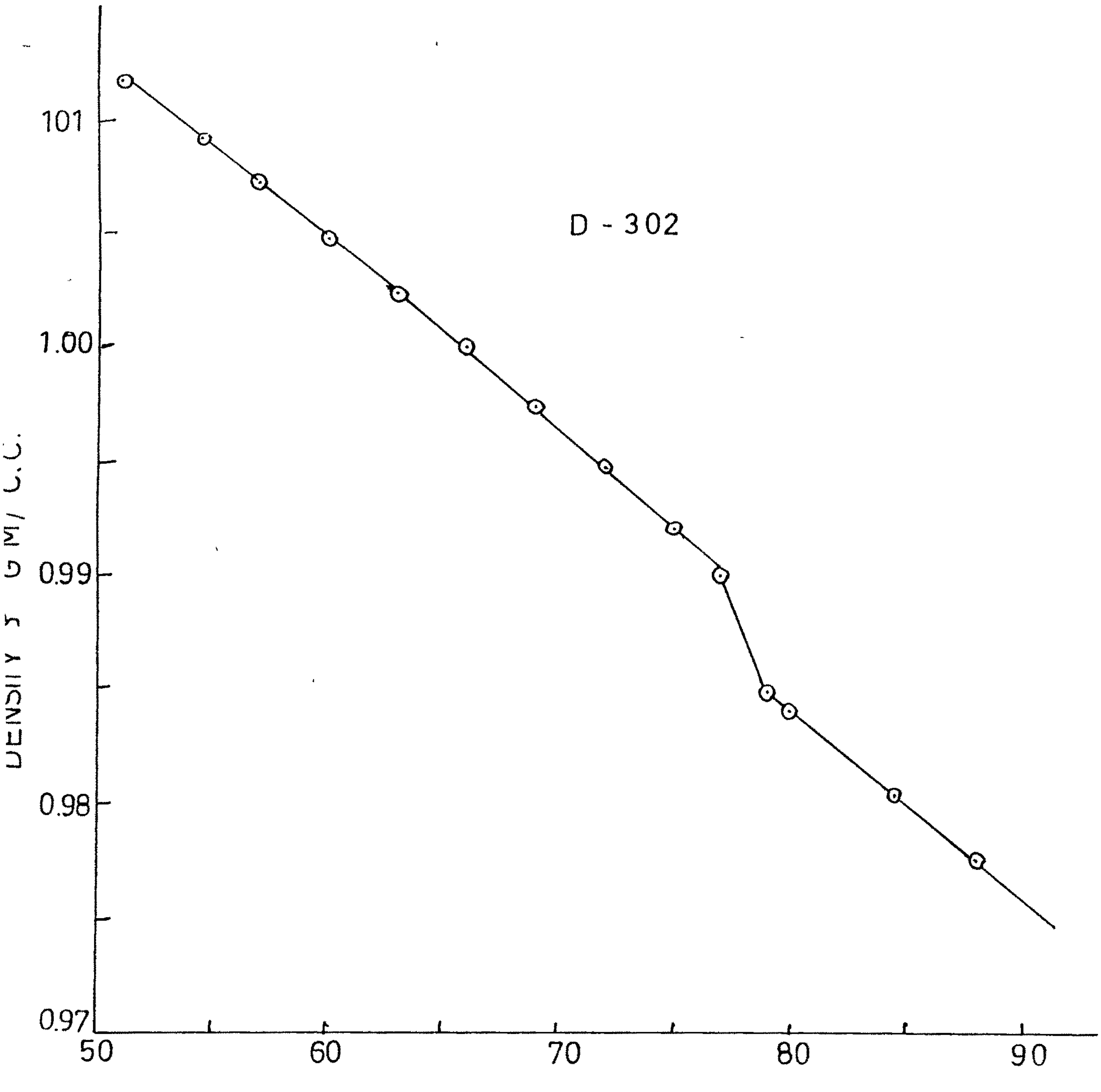


Fig. 2.1 d (i)

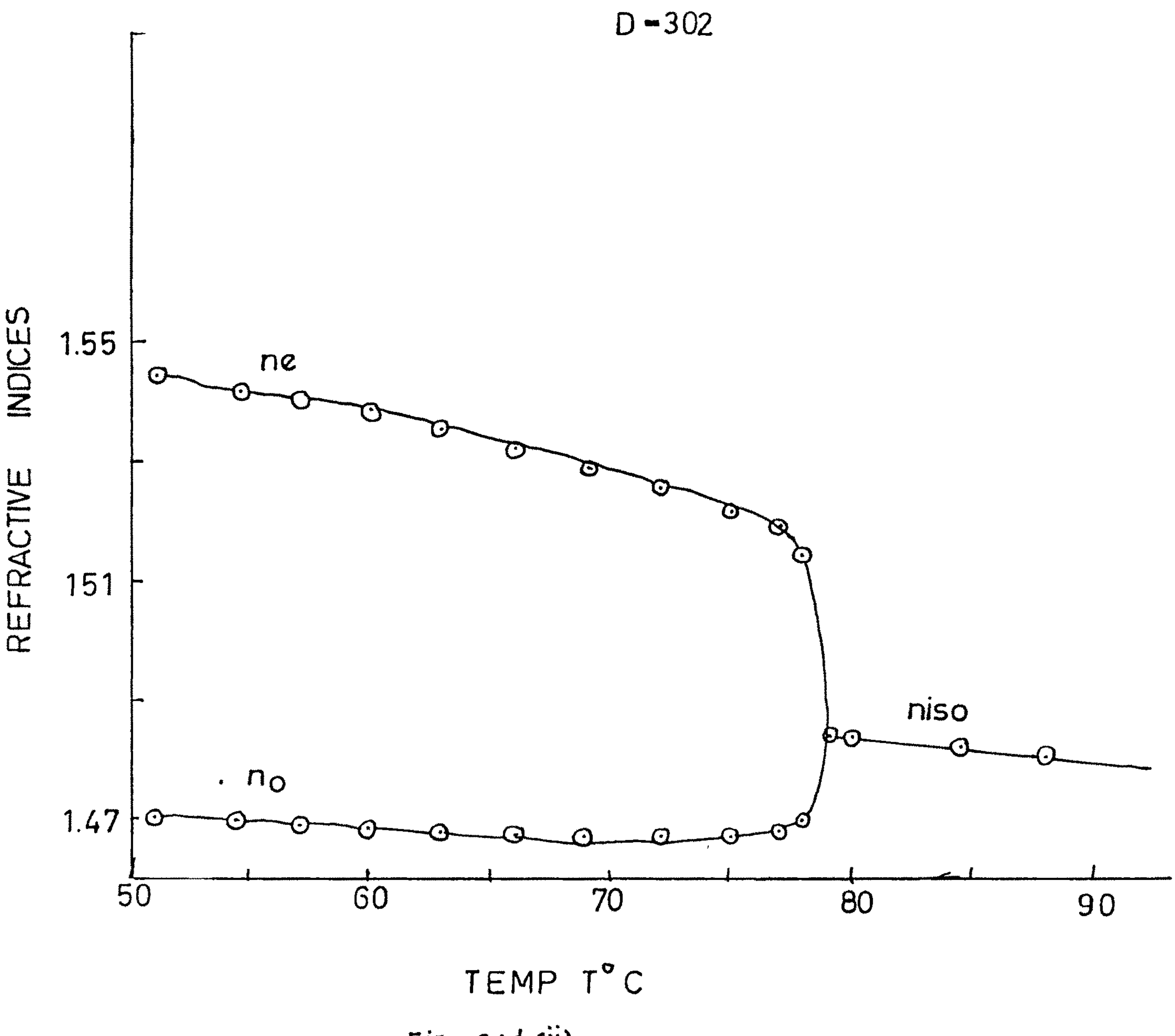

D-302
REFRACTIVE INDICES
1.55
151
1.47
ne
no
niso
50
60
70
80
90
TEMP T°C

Fig. 2.1d (ii).

Table 2.1 (e)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of (D-402)

Temp degree C	ρ gm/cc	n_o	n_e
40	1.0106	1.4730	1.5508
44	1.0072	1.4723	1.5469
45.5	1.0063	1.4712	1.5473
52	1.0012	1.4703	1.5408
55.5	0.9986	1.4695	1.5380
59.5	0.9958	1.4686	1.5345
64	0.9923	1.4685	1.5288
67	0.9897	1.4682	1.5256
69	0.9879	1.4680	1.5234
71	0.9860	1.4680	1.5207
73	0.9841	1.4690	1.5164
74	0.9832	1.4698	1.5137
75.5	0.9815	1.4840	
76.5	0.9791	1.4835	
78	0.9778	1.4828	
80	0.9761	1.4820	

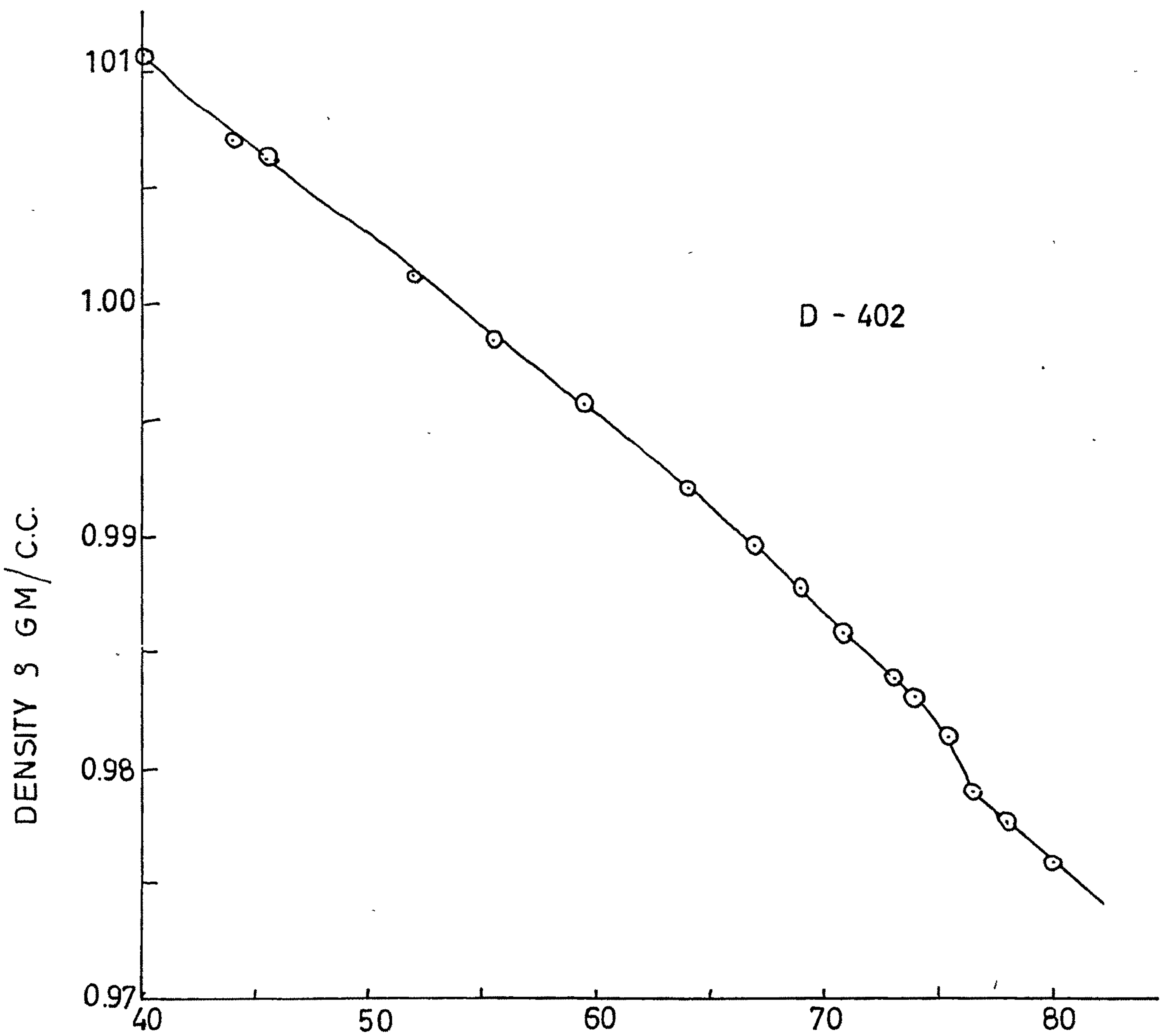


Fig. 2·1 e (i).

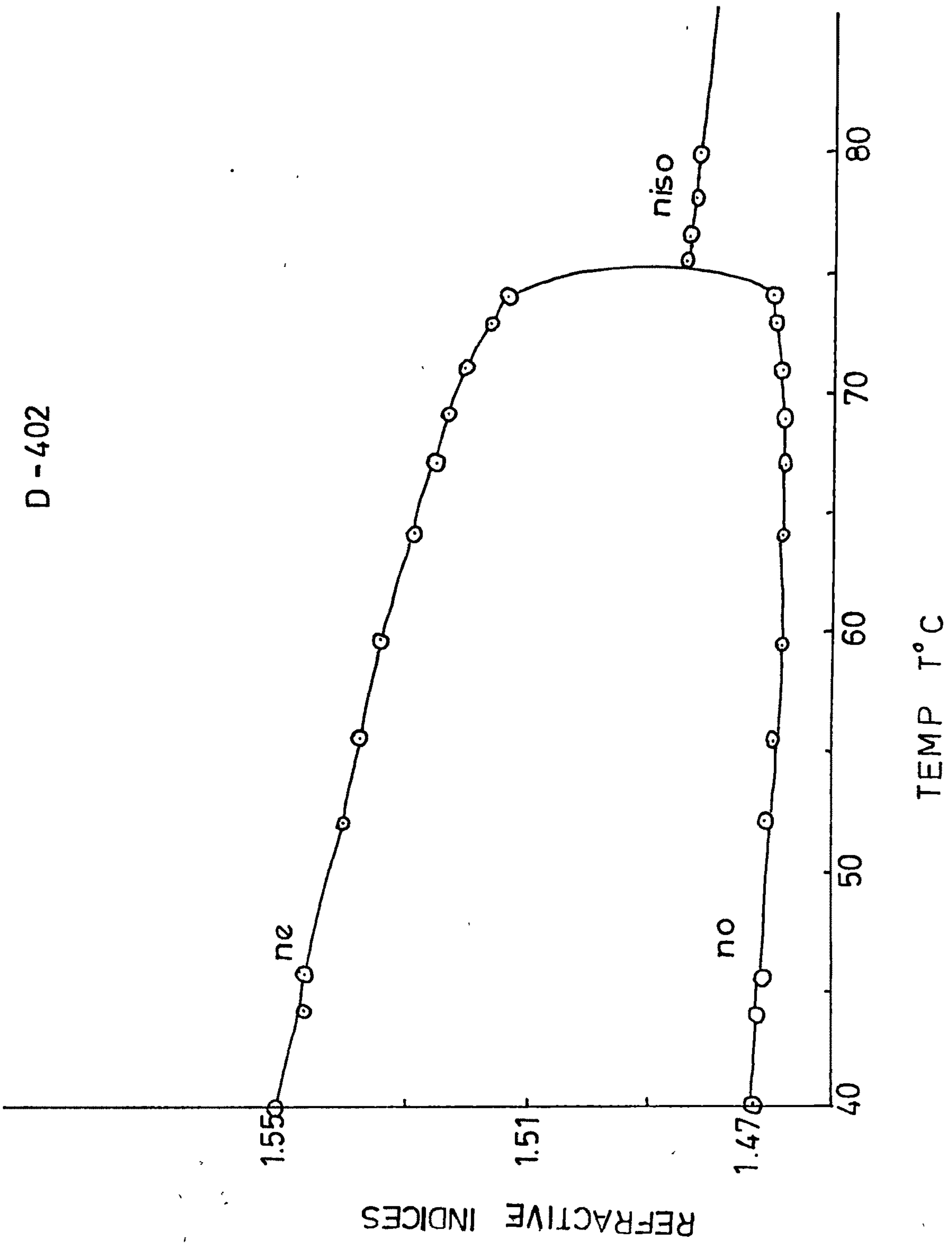

D - 402
niso
ne
no
1.55
1.51
1.47
REFRACTIVE INDICES
40
50
60
70
80
TEMP T°C

Fig 2.1e (ii)

Table 2.1 (f)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of (D 501)

Temp degree C	ρ gm/cc	n_o	n_e
40	1.0164	1.4772	1.5445
50	1.0087	1.4742	1.5389
60.5	1.0068	1.4725	1.5309
65	0.9970	1.4723	1.5256
70	0.9924	1.4732	1.5180
72.5	0.9896	1.4752	1.5112
74.5	0.9861	1.4865	
75.5	0.9854	1.4860	

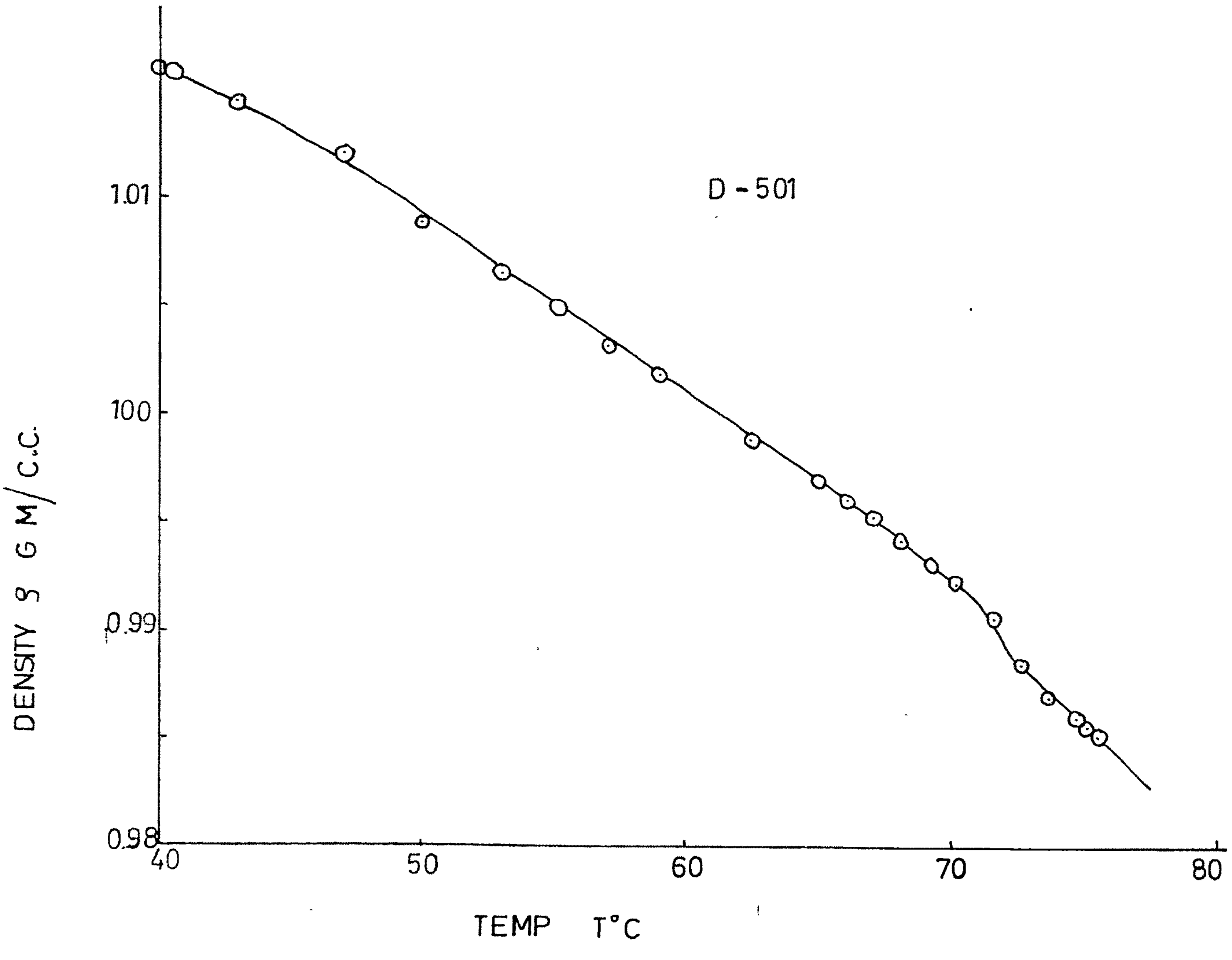


Fig. 2.1 f(i)

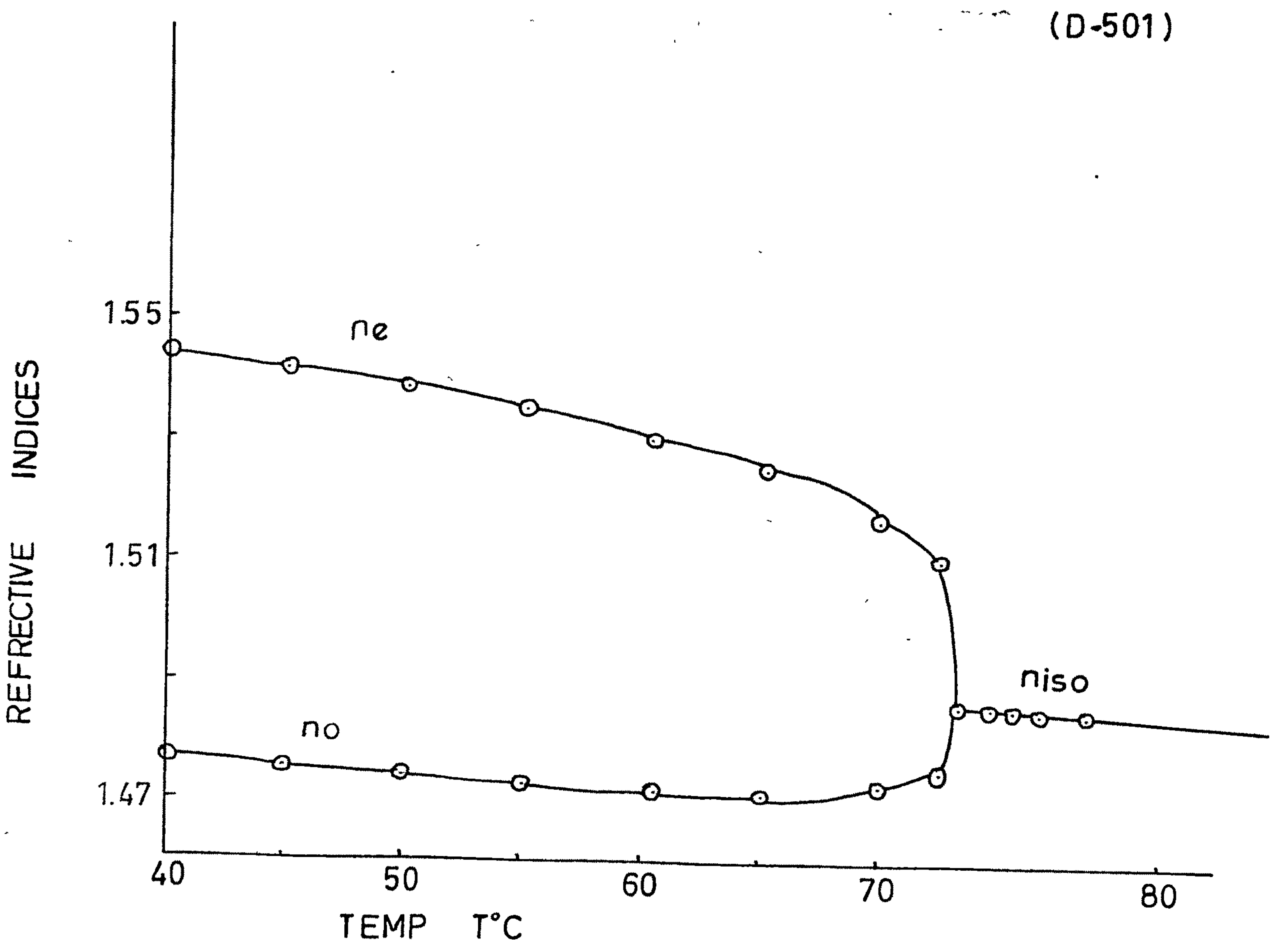
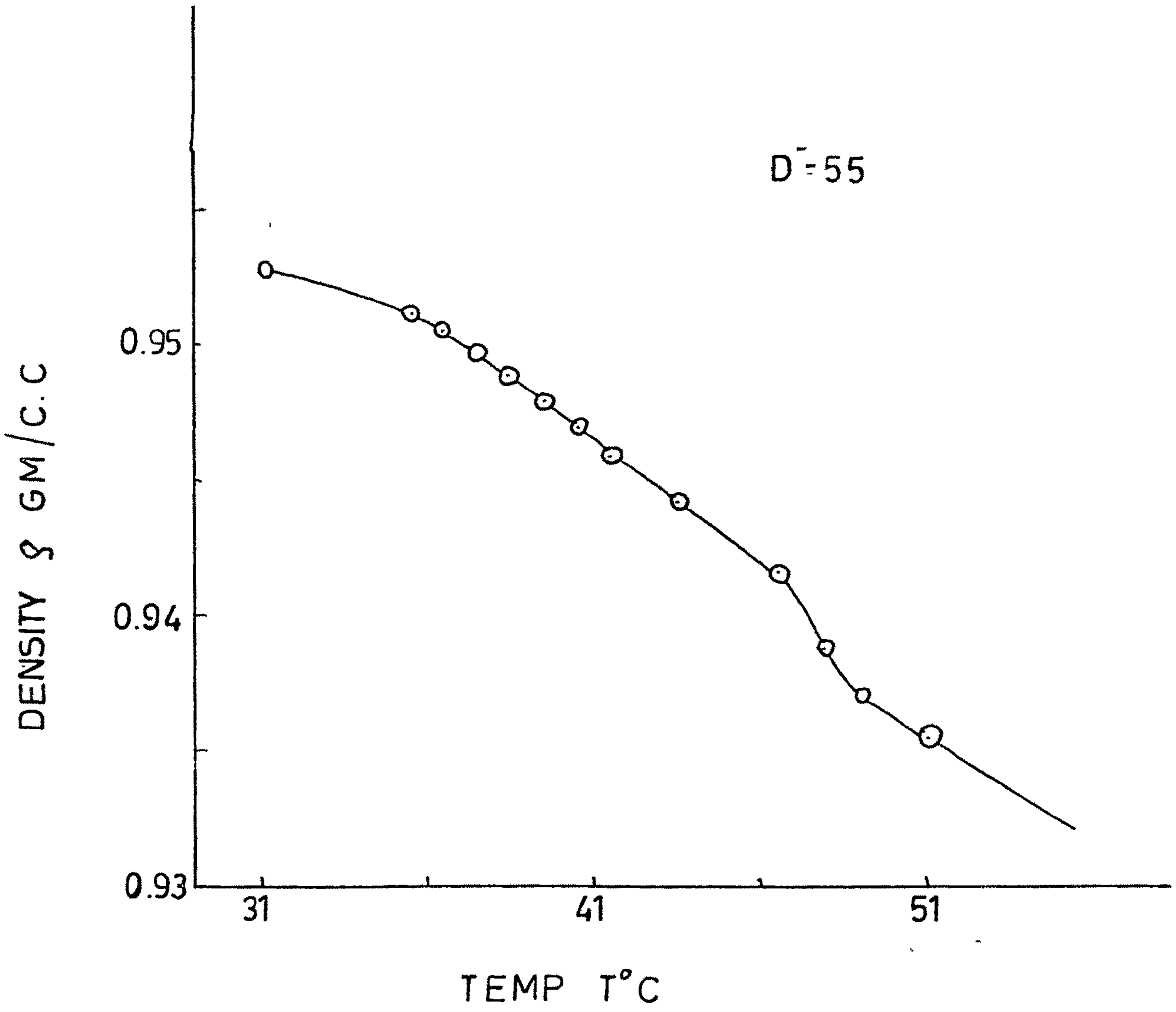

(D-501)
REFRECTIVE INDICES
1.55
1.51
1.47
ne
no
niso
40
50
60
70
80
TEMP T°C

Fig. 2.1f (ii)

Table 2.1 (g)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of D - 55

Temp degree C	ρ gm/cc	n_o	n_e
36	0.9508	1.4730	1.5304
37	0.9501	1.4724	1.5301
39	0.9468	1.4724	1.5272
41	0.9486	1.4720	1.5250
43	0.9449	1.4722	1.5217
45	0.9431	1.4736	1.5163
47	0.9416	1.4870	
48.5	0.9389	1.4862	
51.5	0.9357	1.4848	


D=55
DENSITY ρ GM/C.C
0.95
0.94
0.93
31
41
51
TEMP T°C

(D-55)

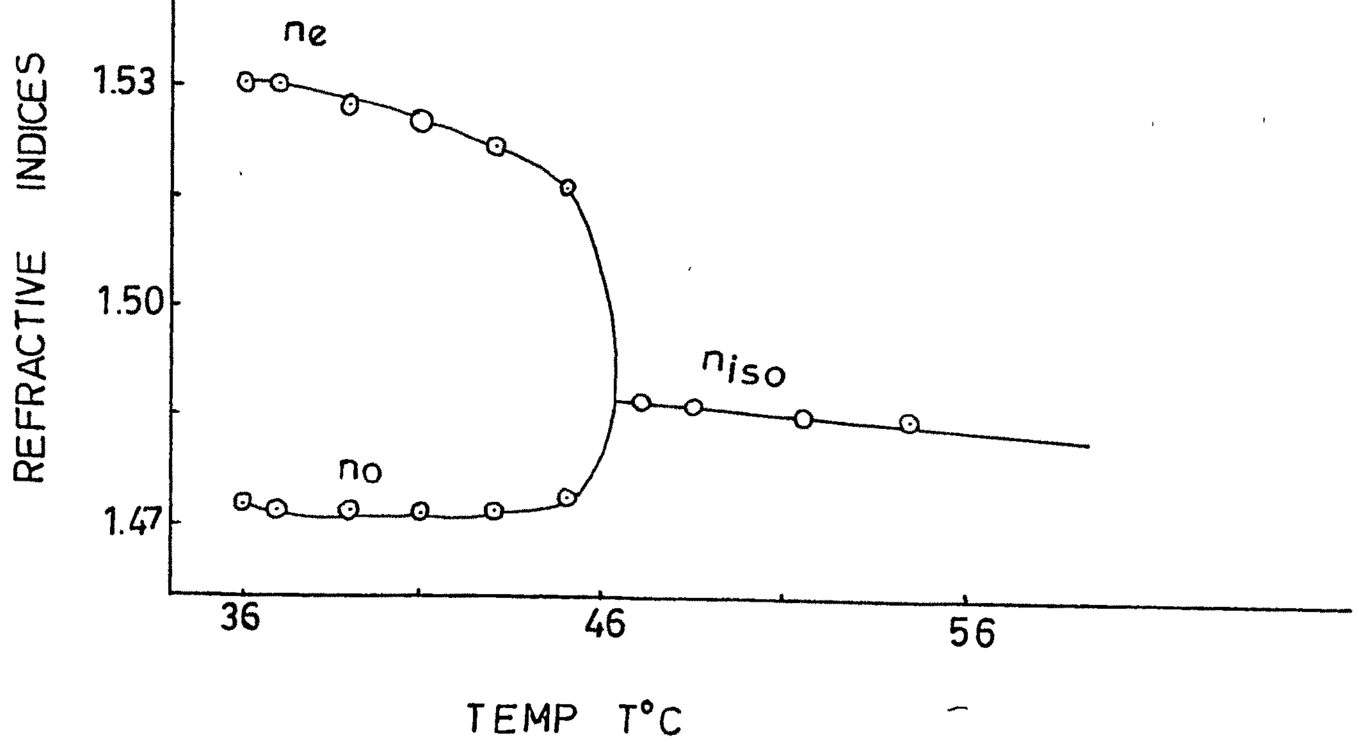


Table 2.1 (h)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of CPBB

Temp degree C	ρ gm/cc	n_o	n_e
80	1.061	1.5476	
74.5	1.065	1.5492	
69	1.070	1.5514	
60.5	1.076	1.5548	
56	1.081	1.5572	
50	1.084	1.5594	
45	1.088	1.5614	
43 iso	1.089	1.5624	
41	1.095	1.5290	1.6294
40	1.095	1.5266	1.6348
39	1.096	1.5250	1.6392
38	1.097	1.5238	1.6423
37	1.098	1.5230	1.6449
36	1.099	1.5222	1.6476
35 nem	1.100	1.5214	1.6505

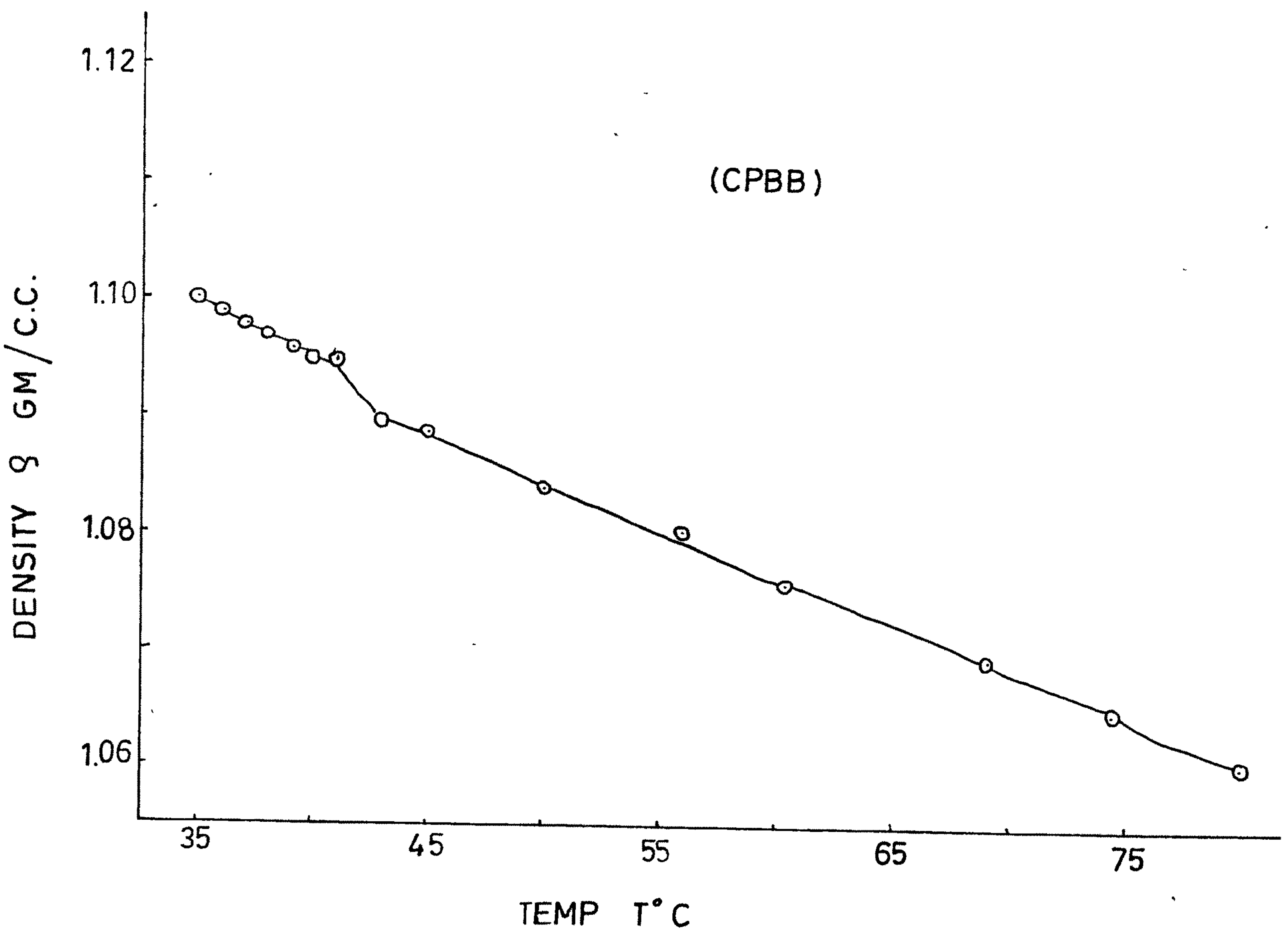


fig. 2·1 h (i)

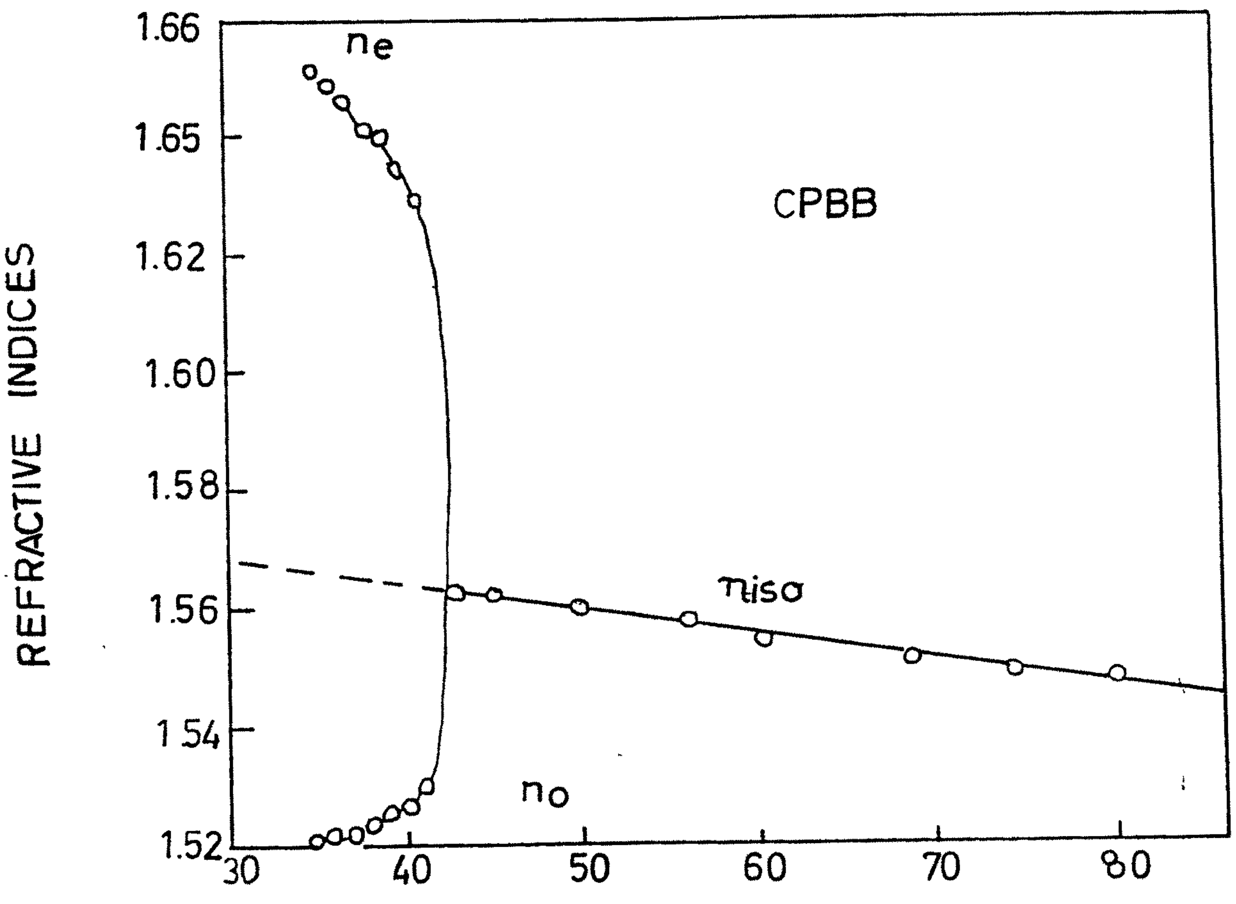

CPBB
ne
no
niso
TEMPt° c
REFRACTIVE INDICES
1.66
1.65
1.62
1.60
1.58
1.56
1.54
1.52
30
40
50
60
70
80

Fig2·1 h(ii)

Table 2.1 (i)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of CPPOB

Temp degree C	ρ gm/cc	n_o	n_e
88.5	1.073	1.5450	
85.5	1.075	1.5460	
82.5	1.078	1.5475	
79.5	1.080	1.5486	
74	1.083	1.5123	1.6256
72	1.090	1.5105	1.6309
69	1.093	1.5082	1.6389
65.5	1.096	1.5070	1.6482
62.5	1.099	1.5065	1.6505
59	1.102	1.5060	1.6565
55.5	1.106	1.5055	1.6599
52.5	1.109	1.5048	1.6649
49	1.112	1.5040	1.6708

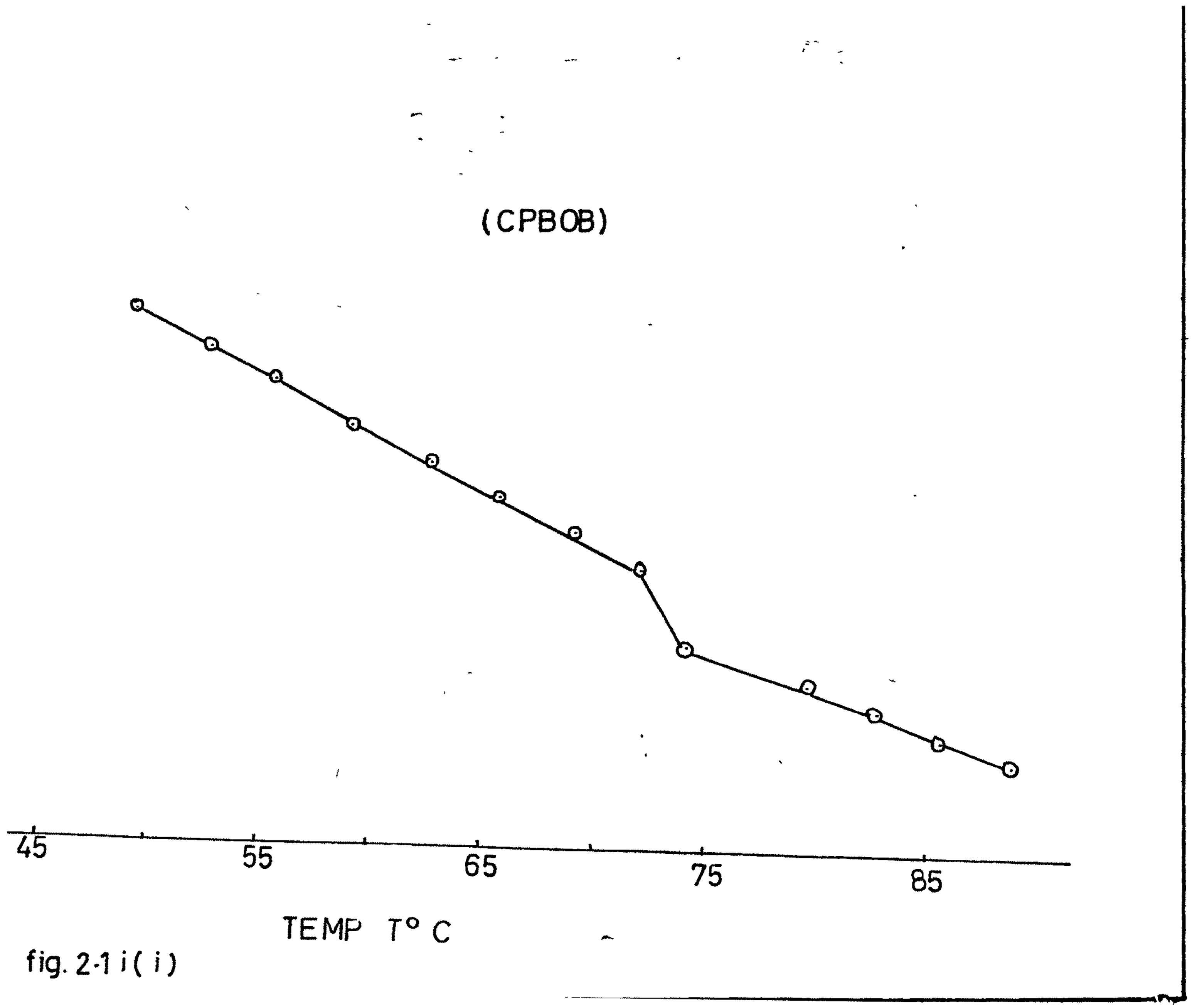


fig. 2·1 i(i)

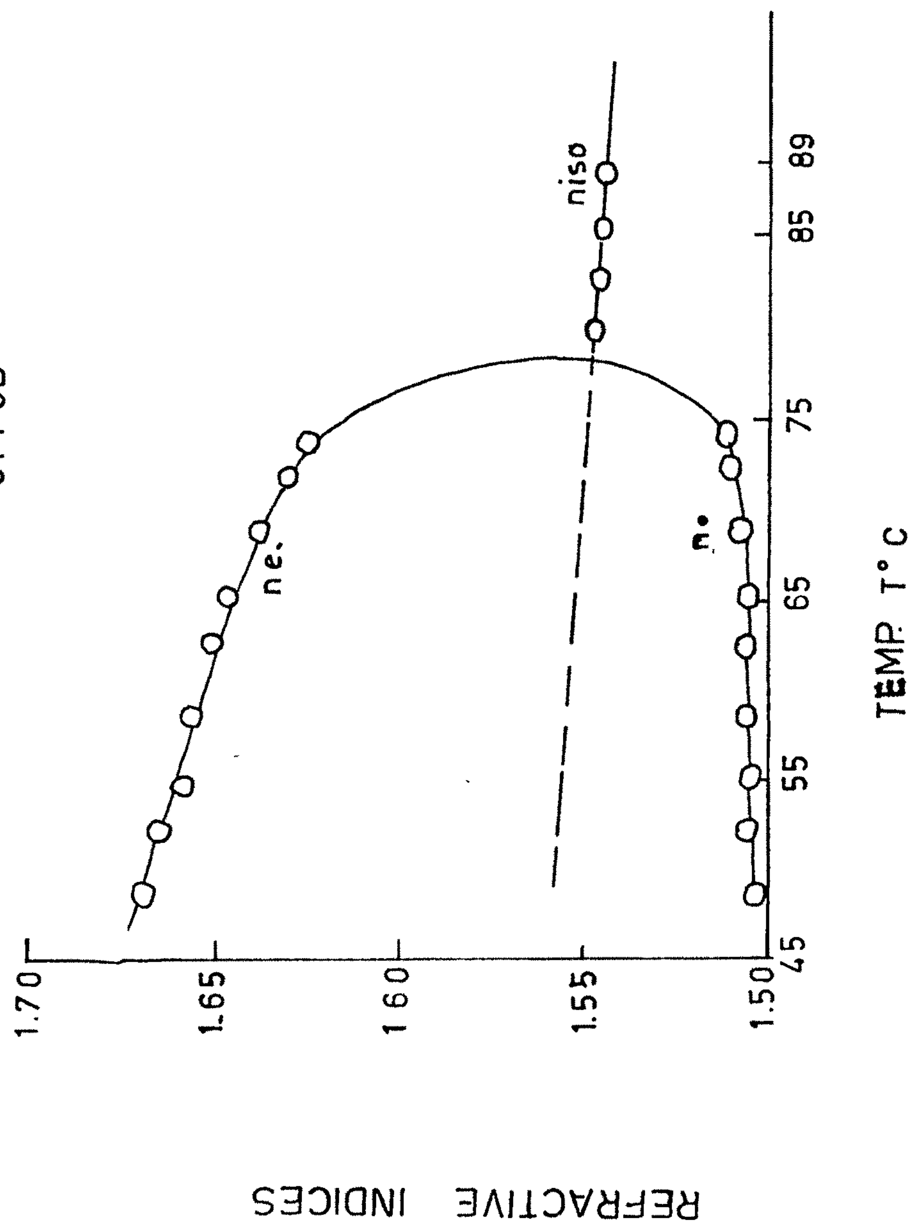

CPPOB
ne.
no
niso
1.70
1.65
1.60
1.55
1.50
45
55
65
75
85
89
TEMP. T°C
REFRACTIVE INDICES

Fig 2.1i (ii)

Table 2.1 J

Temperature variation density (s) and refractive indices n_o, n_e and n_{iso} of E - 4

Temp degree C	s gm/cc	no	ne
38	1.0221	1.5162	1.6993
43	1.0175	1.5174	1.6899
47	1.0140	1.5182	1.6829
50	1.0110	1.5190	1.6758
53	1.0084	1.5202	1.6708
56	1.0054	1.5228	1.6618
59	1.0028	1.5272	1.6486
62	0.9968	1.5675	
63	0.9960	1.5672	
65	0.9939	1.5656	
68	0.9917	1.5640	
71	0.9890	1.5634	

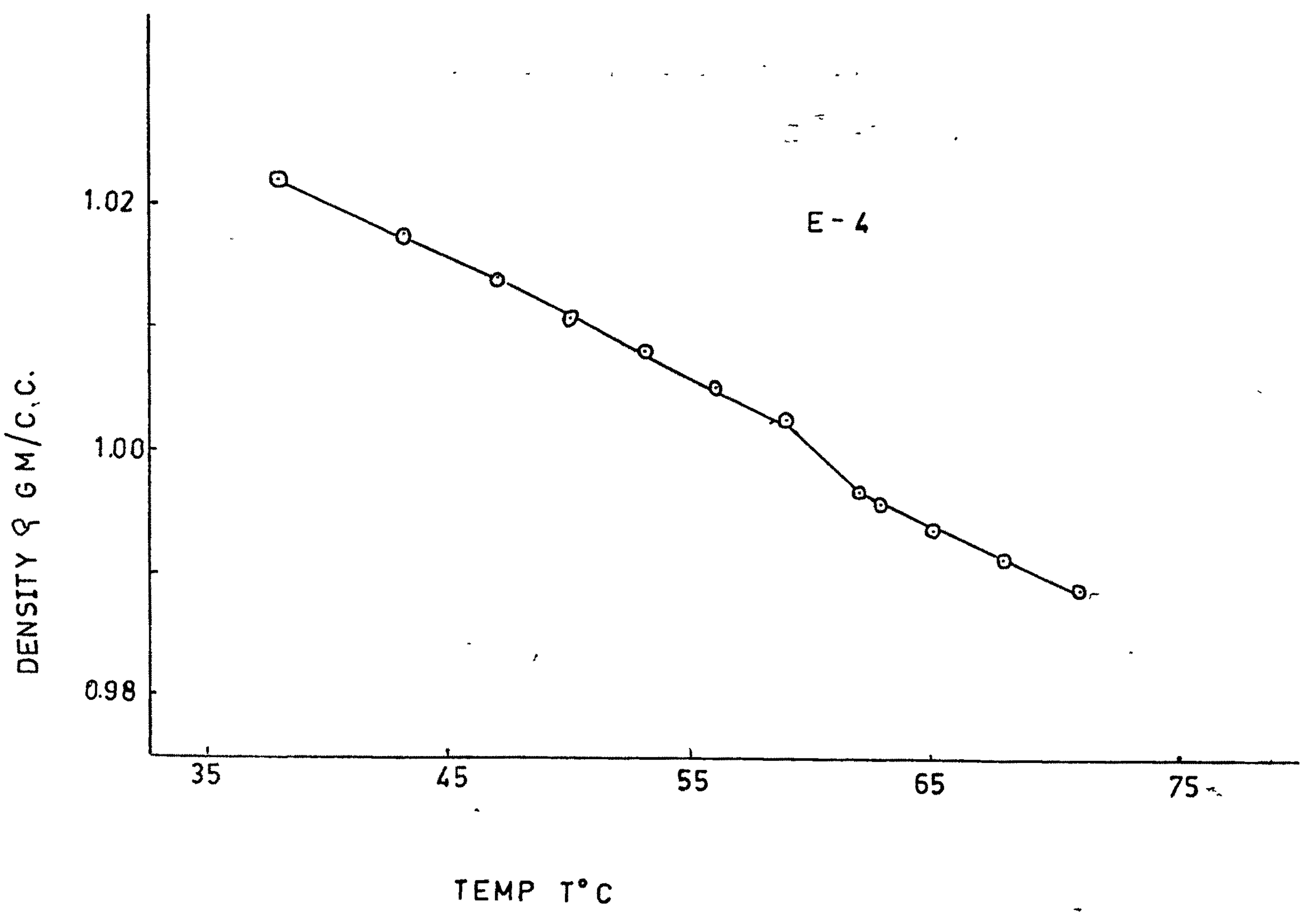


fig.2.T i(i)

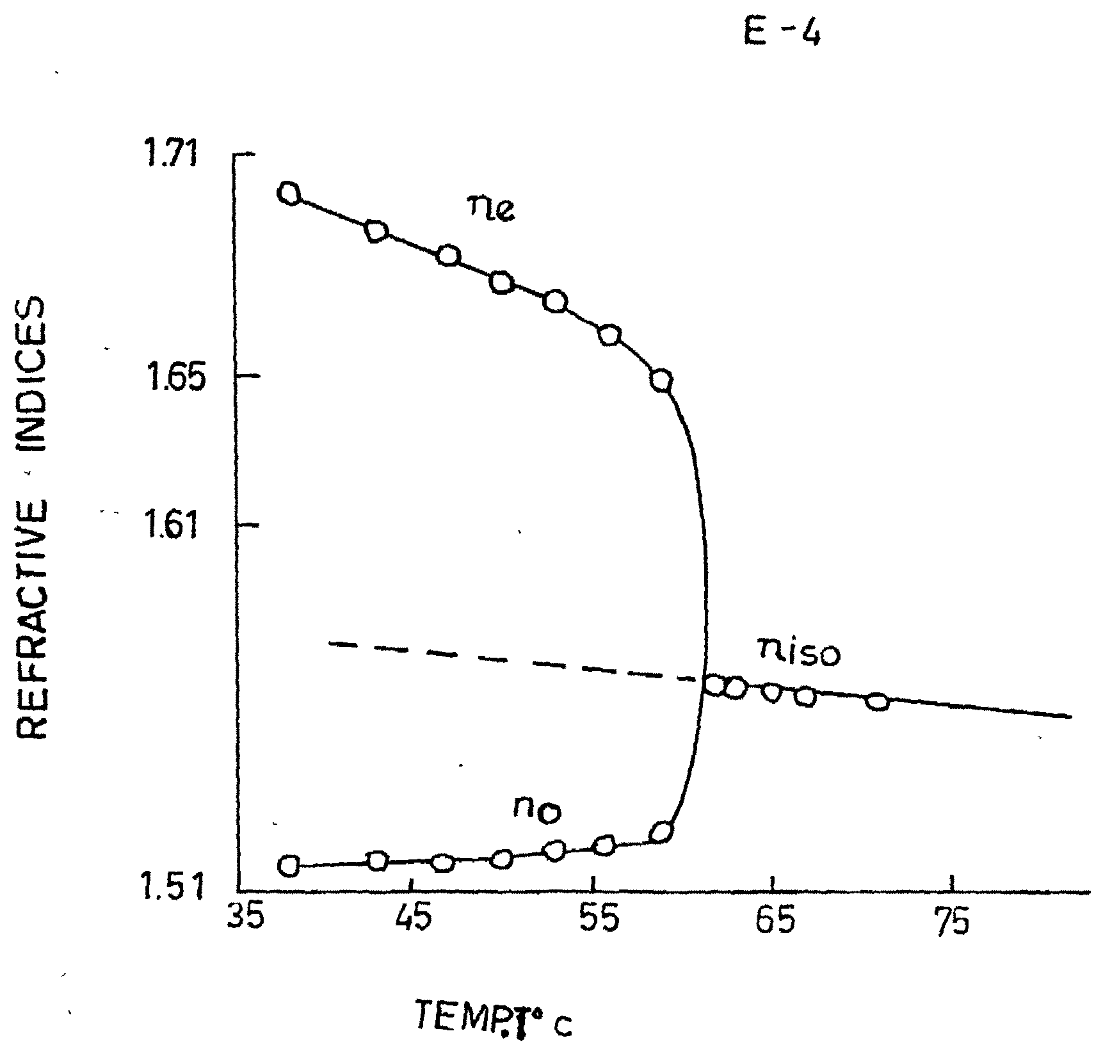

E - 4
REFRACTIVE · INDICES
1.71
1.65
1.61
1.51
ne
niso
no
35
45
55
65
75
TEMP.T° c

Fig 2·1 j(ii)

Table 2.1k

Temperature variation of density (s) and refractive indices n_e, n_o and n_{iso} of E - 7

Temp degree C	s gm/cc	no	ne
24	1.0337	1.5220	1.7234
27	1.0308	1.5220	1.7193
30	1.0285	1.5224	1.7144
33	1.0259	1.5230	1.7092
36	1.0232	1.5234	1.7051
39	1.0205	1.5238	1.6999
42	1.0176	1.5250	1.6930
45	1.0148	1.5252	1.6898
48	1.0117	1.5265	1.6861
51	1.0088	1.5282	1.6771
54	1.0056	1.5315	1.6671
56	1.0036	1.5355	1.6568
60	0.9968	1.5755	
61	.9960	1.5745	
64	0.9929	1.5730	
67	0.9904	1.5718	
70	0.9877	1.5708	

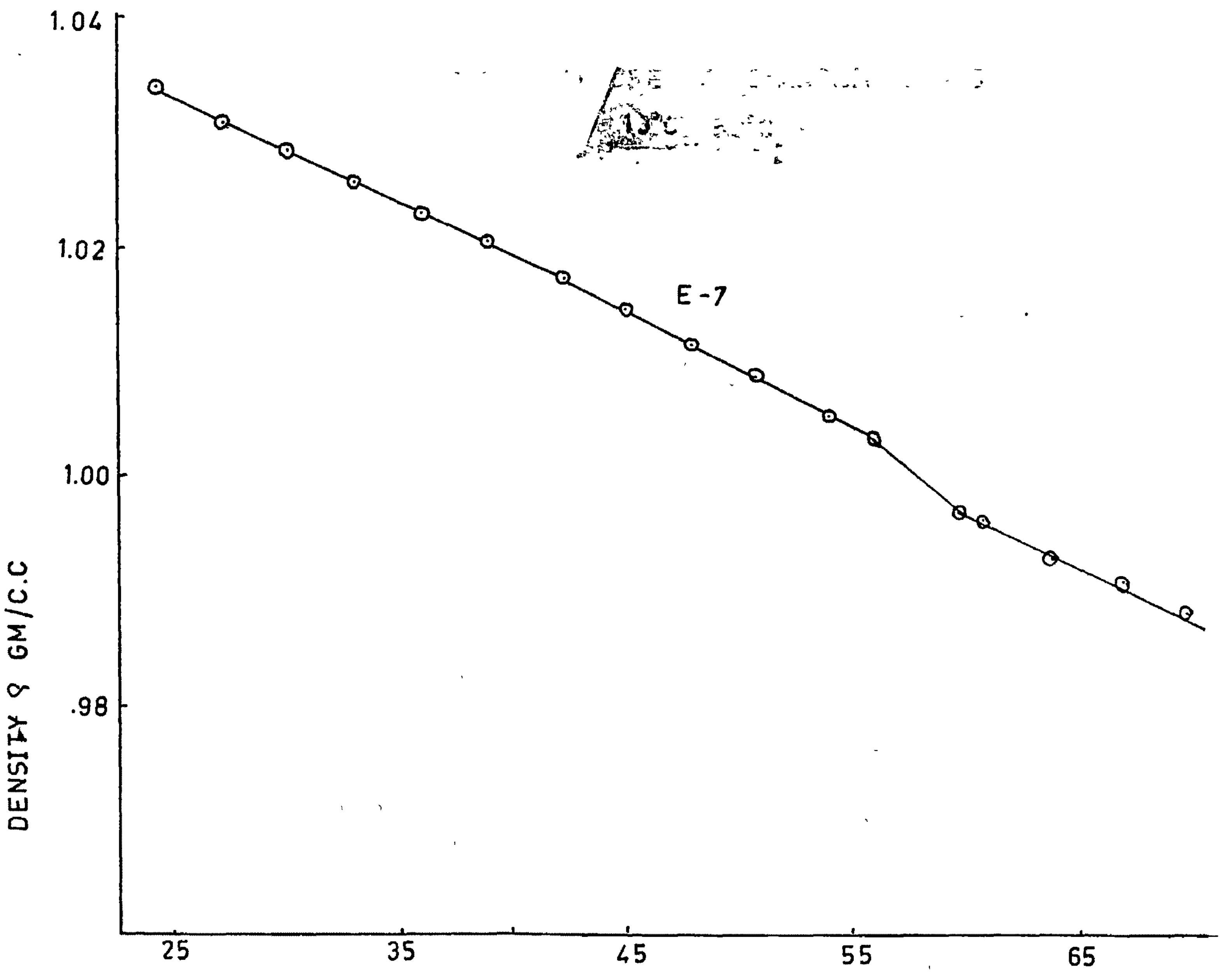


fig. 2·1k(i)

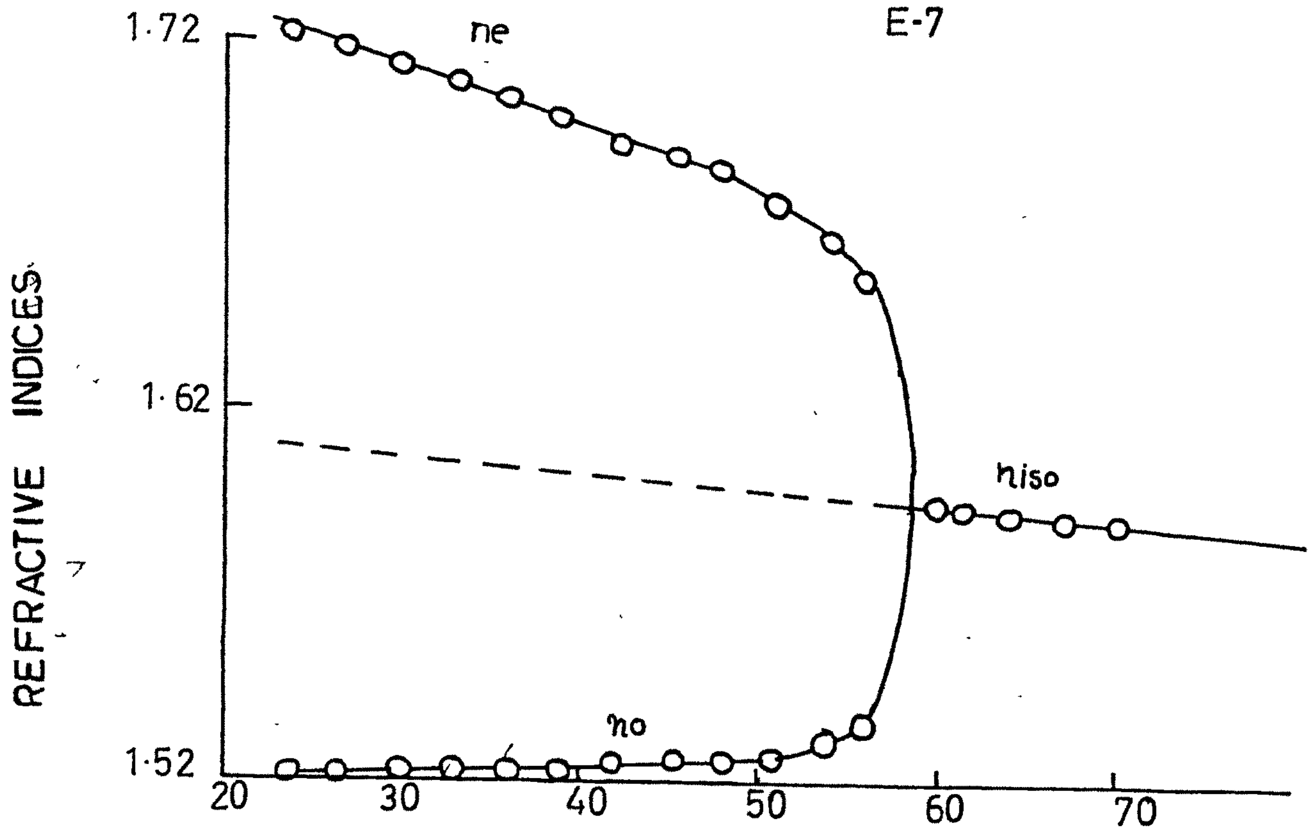


Fig. 2·1k(ii)

Table 2.1(1)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of CCH - 2.

Temp degree C	ρ gm/cc	n_o	n_e
46	0.9250	1.4661	1.4959
46.5	0.9241	1.4661	1.4953
47	0.9232	1.4662	1.4942
47.5	0.9234	1.4663	1.4934
48	0.9220	1.4668	1.4919
49 iso	0.9185	1.4748	
49.5	0.9181	1.4746	
50	0.9178	1.4742	
50.5	0.9174	1.4741	
51	0.9167	1.4740	
53.5	0.9150	1.4729	
55.5	0.9133	1.4720	

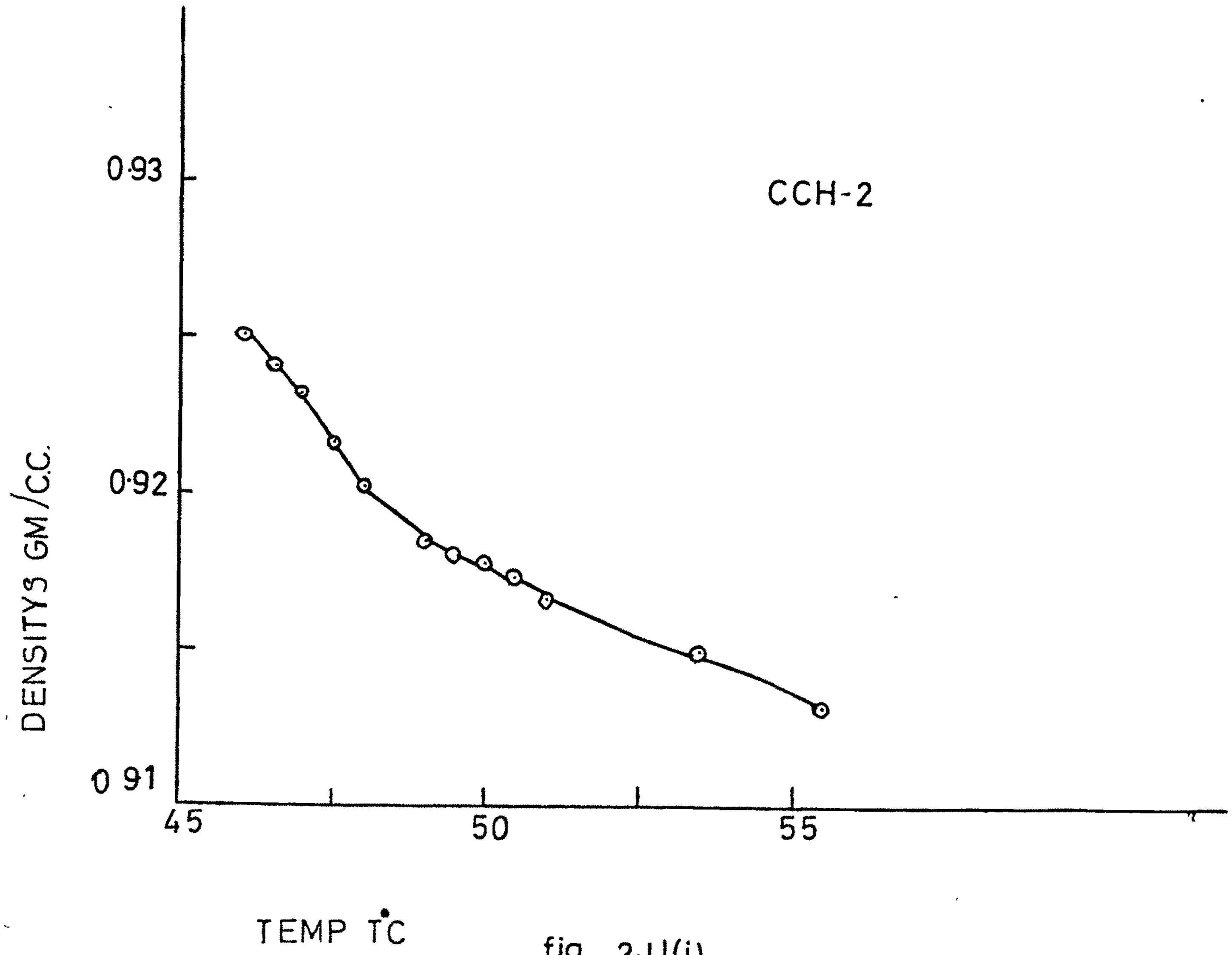
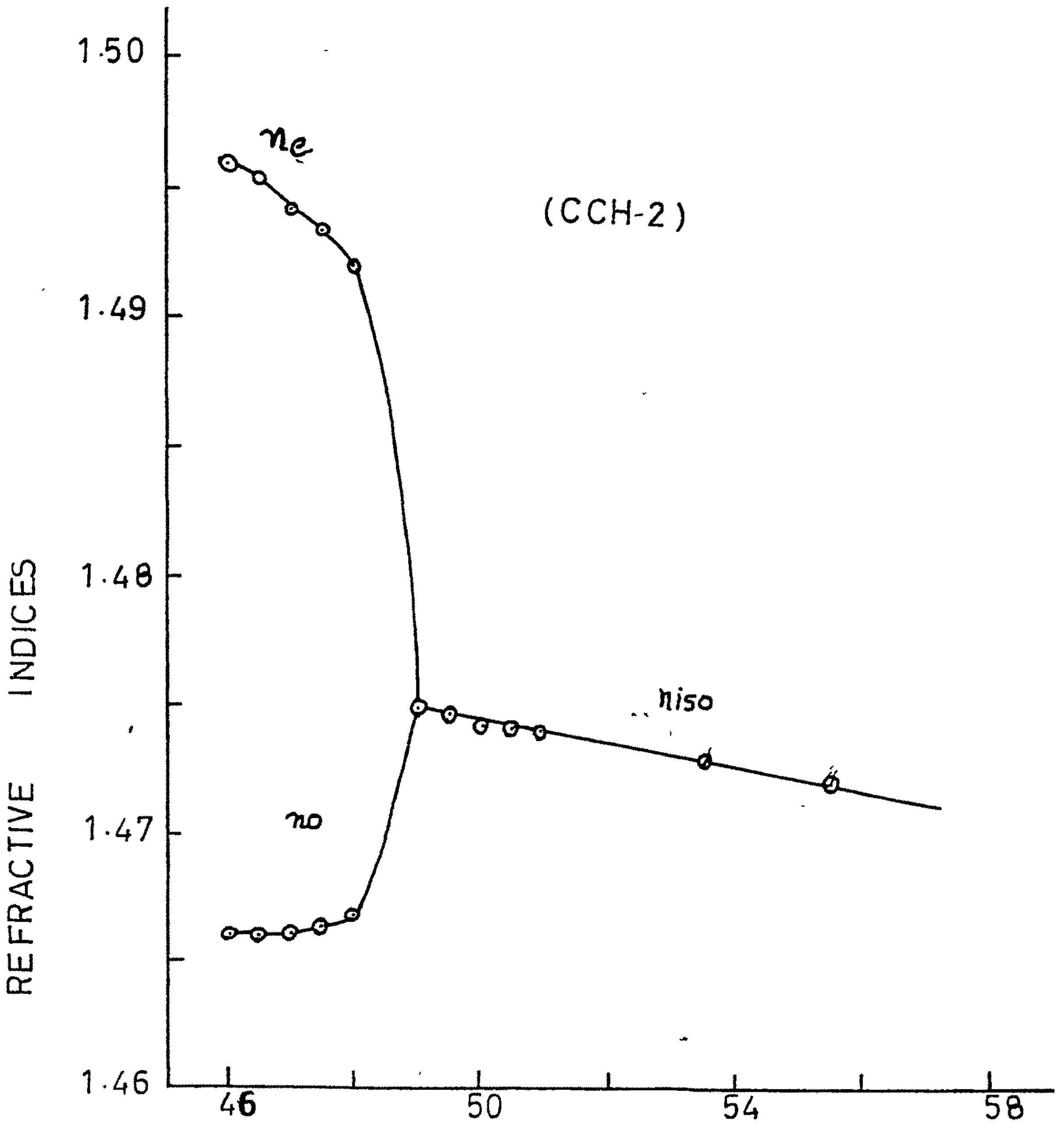


fig. 2·11(i)

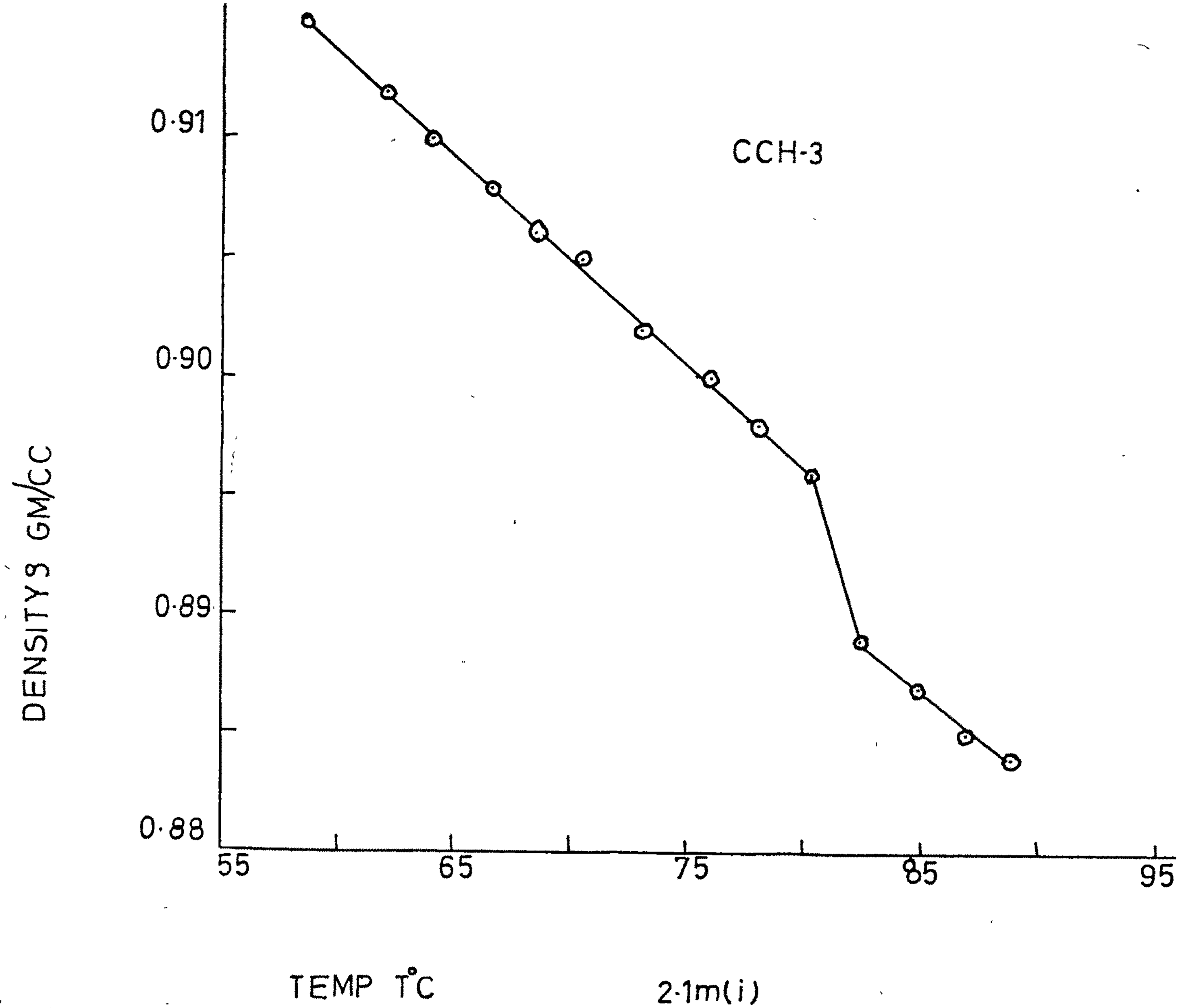

(CCH-2)
n_e
n_o
n_{iso}
1·50
1·49
1·48
1·47
1·46
REFRACTIVE INDICES
46
50
54
58
TEMP T°C.

2·1l(ii)

Table 2.1 (m)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of C C H – 3.

Temp degree C	ρ gm/cc	n_o	n_e
58.5	0.915	1.4590	1.5056
62	0.912	1.4578	1.5029
64	0.910	1.4575	1.5014
66.5	0.908	1.4567	1.4991
68.5	0.906	1.4564	1.4968
70.5	0.905	1.4560	1.4949
73	0.902	1.4553	1.4930
76	0.900	1.4546	1.4900
78	0.898	1.4545	1.4878
80.5	0.896	1.4548	1.4834
82.5 iso	0.889	1.4635	
85	0.887	1.4625	
87	0.885	1.4615	
89	0.884	1.4605	



2·1m(i)

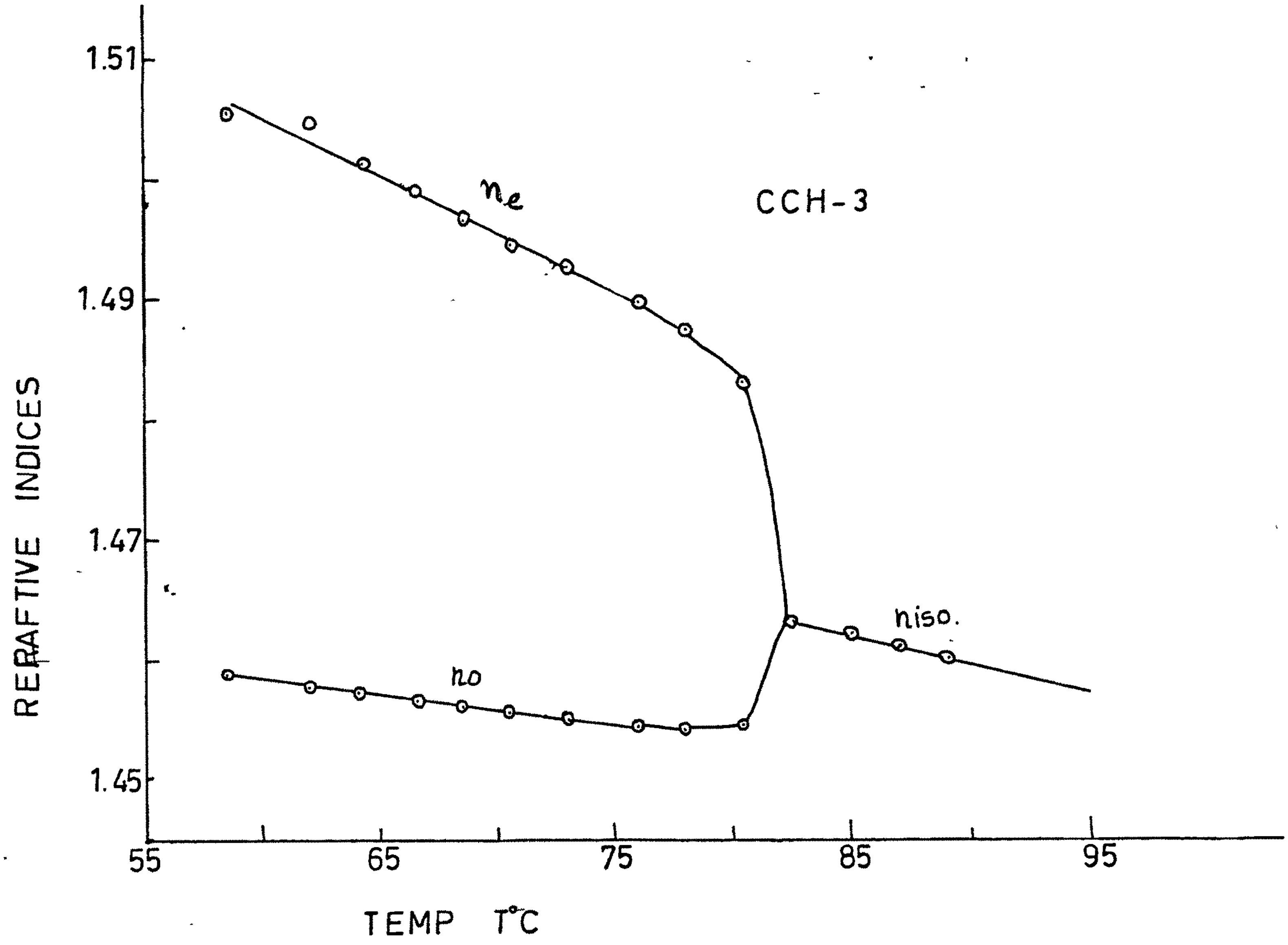

CCH-3
n_e
n_o
niso.
1.51
1.49
1.47
1.45
REFRACTIVE INDICES
55
65
75
85
95
TEMP T°C

fig. 2·1 m(ii).

Table 2.1 (n)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of C C H – 5.

Temp degree C	ρ gm/cc	n_o	n_e
65	0.9080	1.4600	1.5095
68	0.9055	1.4580	1.5093
72	0.9020	1.4568	1.5061
76	0.8983	1.4560	1.5020
78	0.8965	1.4560	1.4991
81	0.8940	1.4568	1.4937
83	0.8920	1.4575	1.4894
85 iso		1.4675	
86		1.4665	
87		1.4660	
88		1.4655	
89	0.8815	1.4650	
92	0.8795	1.4640	

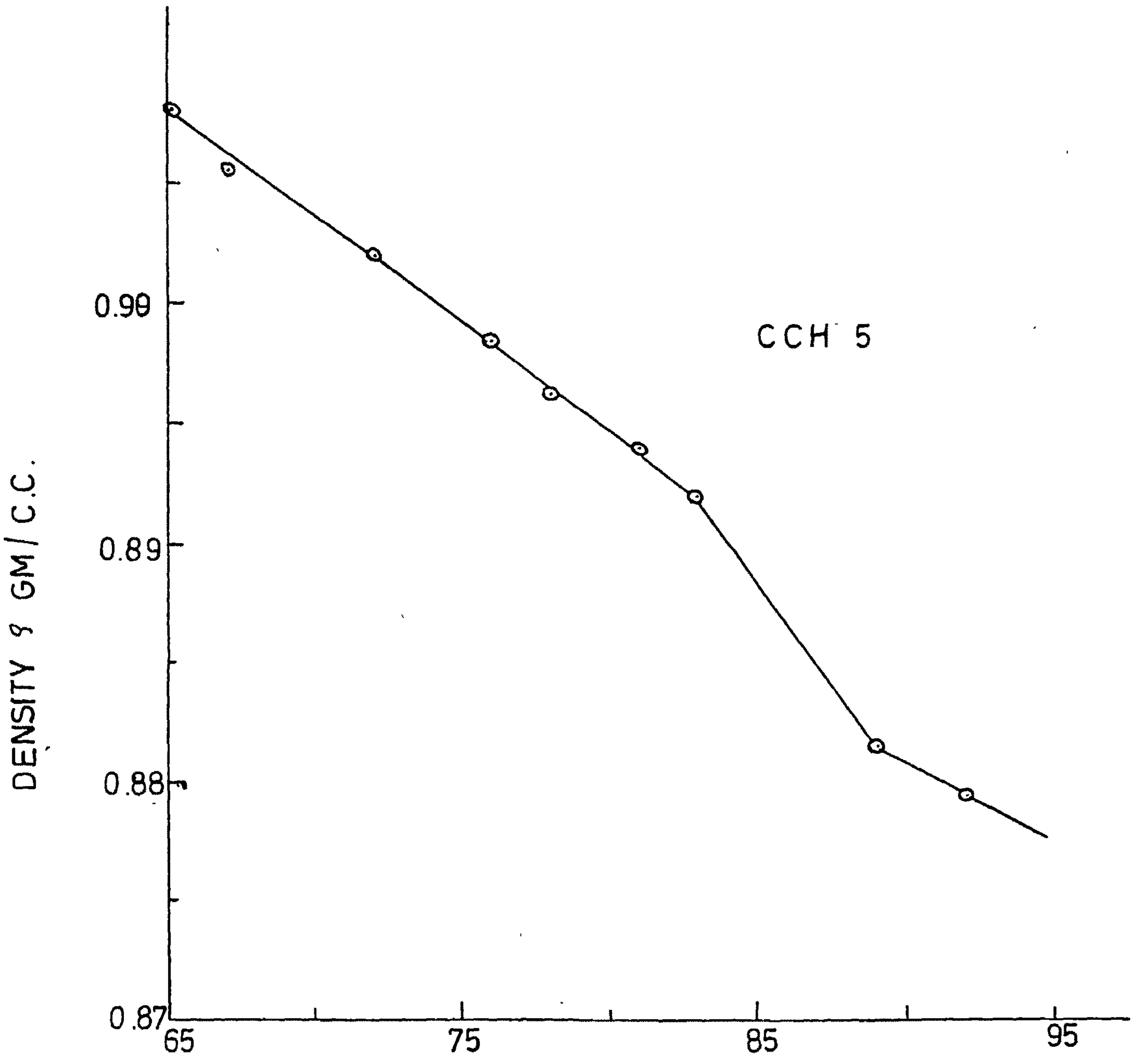


fig. 2·1 n(i)

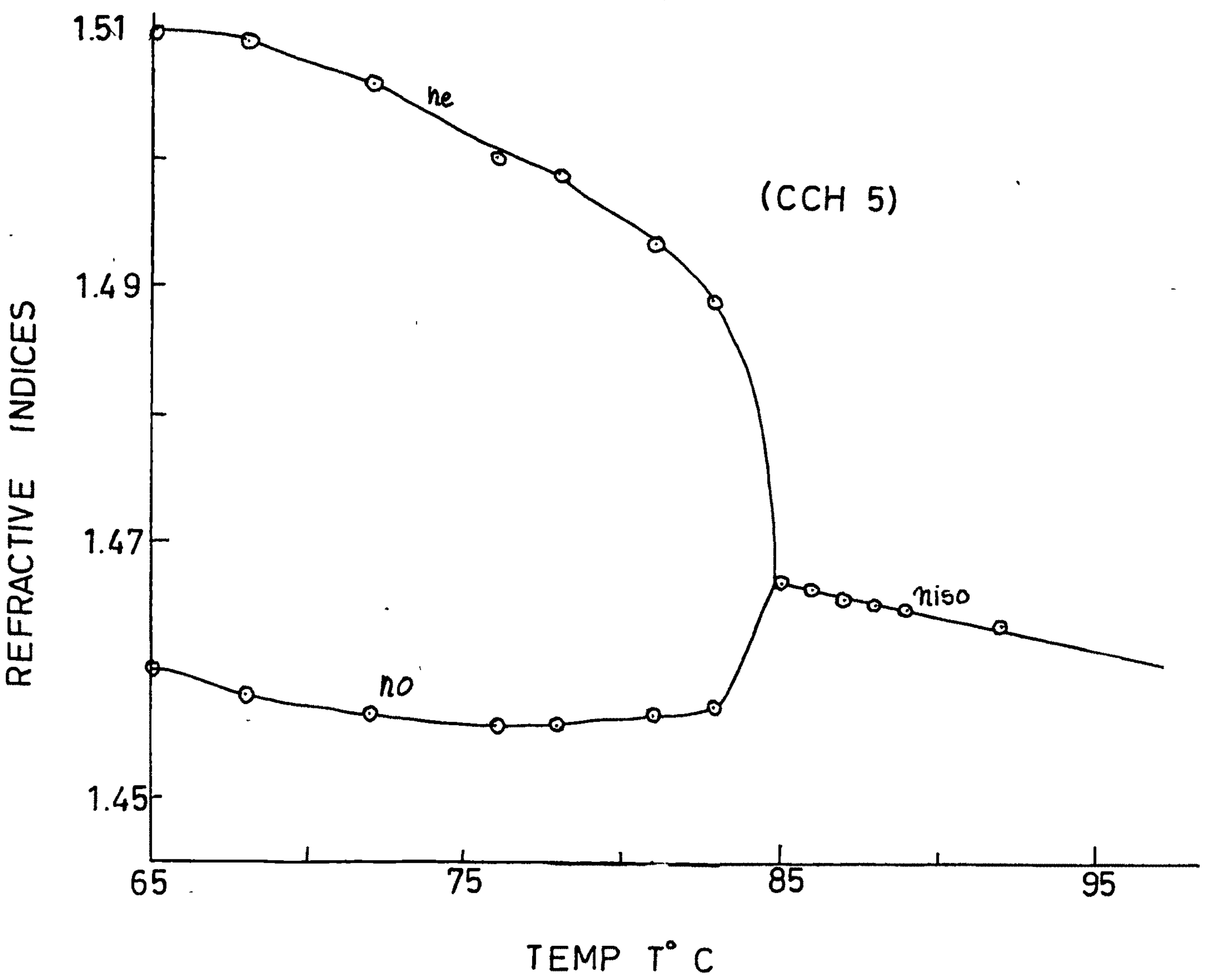

(CCH 5)
ne
no
niso
1.51
1.49
1.47
1.45
65
75
85
95
REFRACTIVE INDICES
TEMP T° C
fig. 2.1 n (ii)

Table 2.1 (o)

Temperature variation of density (ρ) and refractive indices n_o, n_e and n_{iso} of CCH - 7.

Temp degree C	ρ gm/cc	n_o	n_e
71	0.8928	1.4558	1.5009
72	0.8921	1.4554	1.4997
73	0.8910	1.4552	1.4980
74	0.8901	1.4550	1.4966
75	0.8891	1.4548	1.4952
76	0.8880	1.4546	1.4936
77	0.8873	1.4544	1.4919
78	0.8862	1.4542	1.4905
79	0.8849	1.4540	1.4891
80	0.8837	1.4538	1.4874
81	0.8825	1.4537	1.4859
84 iso	0.8768	1.4625	
85	0.8760	1.4620	
87	0.8746	1.4604	
89	0.8730	1.4592	
91	0.8717	1.4590	

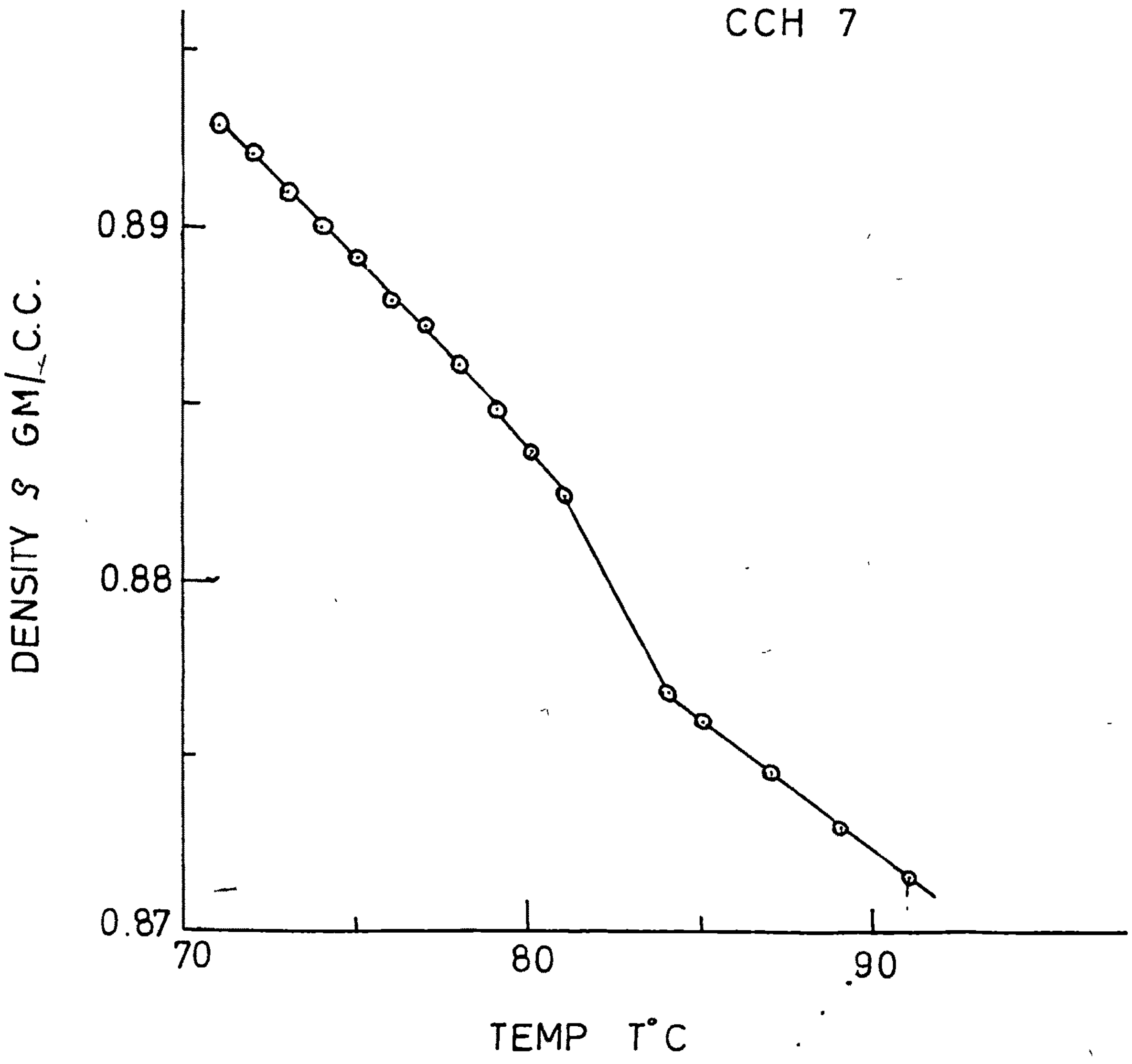
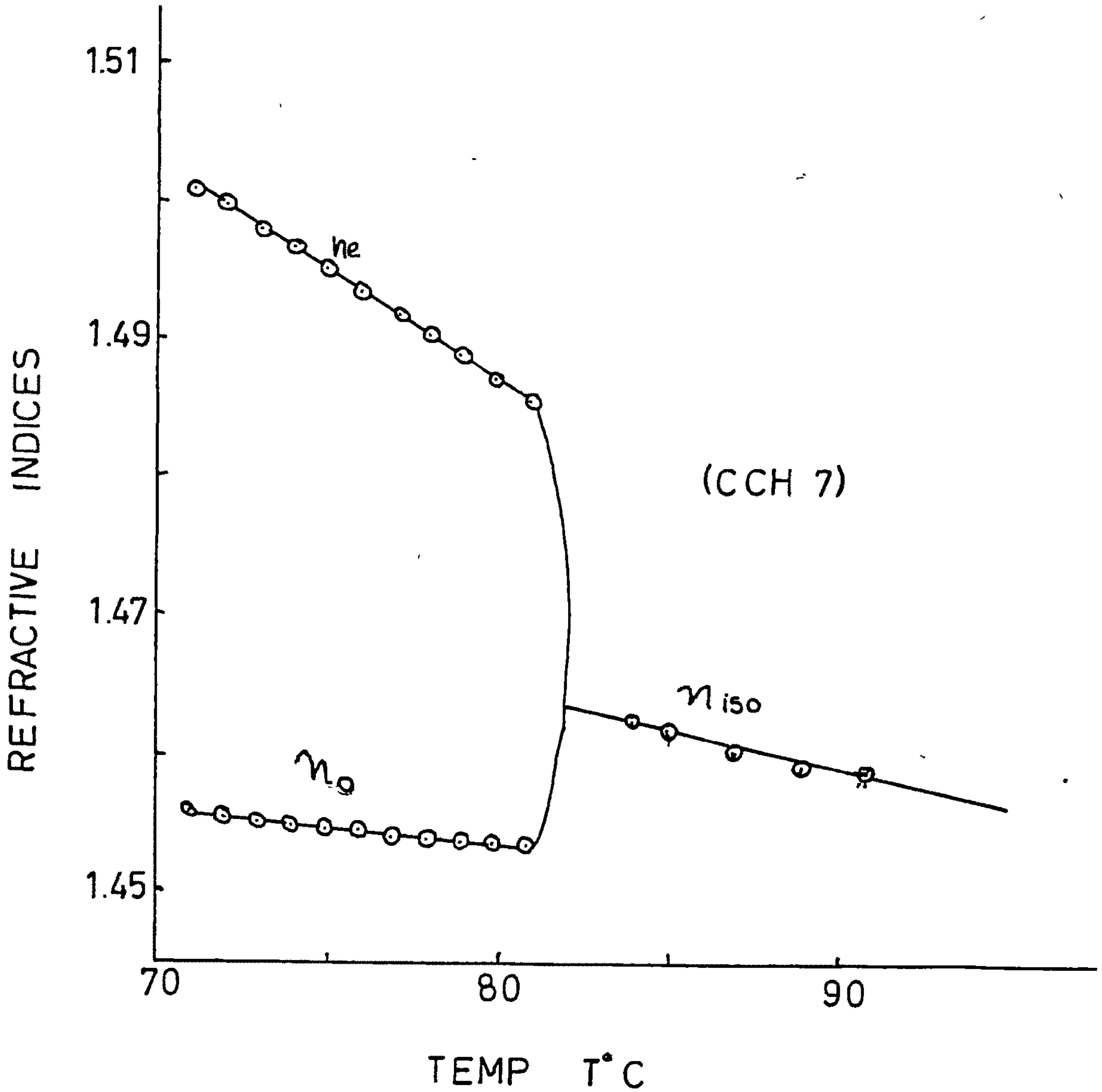


fig. 2.20 (i)


REFRACTIVE INDICES
1.51
1.49
1.47
1.45
70
80
90
TEMP T°C
ne
no
niso
(CCH 7)
fig. 2·2 0(ii)

transition.

Temperature variation of Refractive indices in the Liquid crystals.

Figures 2.1 a (ii) to 2.10 (ii) show the temperature variation of ne, no and n in the liquid crystal samples studied. From the figures it is observed that in general the extrodinary refractive index n_e increases with decrease in temperature while the ordinary refractive index n_o decreases with a decrease in temperature in the nematic phase. In the isotropic phase the refractive index n decreases with an increase in temperature as in normal organic liquid.

Temperature variation of Principal Polarizabilities α_e, α_o and order parameter (S).

The order parameter S can be determined and its temperature variation studied if the principal polarizabilities α_e and α_o are known as a function of temperature. The determination of α_e and α_o from n_o & n_e require the knowledge of the local field inside the medium. The author has computed the principal polarizabilities by Vuk's and Neugebauer's approach.

If we assume that the local field is isotropic as assumed by Vuk's[8] we have the effective polarizalities.

$$\alpha_{e,o} = \frac{3}{4\pi N}\left(\frac{n_{e,o}^2 - 1}{\bar{n}^2 + 2}\right) \cdots\cdots (4) \qquad \bar{n}^2 = \frac{1}{3}\left(n_e^2 + 2n_o^2\right) \qquad N = \frac{N_o \rho}{M}$$

Where N is the number of molecules per cm^3, No is the Avogadro's number, ρ the density and M the molecular weight.

If the internal field is assumed to be anisotropic, then from Neugebauer's derivation.

$$\eta_{e,o}^2 - 1 = \frac{4\pi N \alpha_{e,o}}{1 - N \alpha_{e,o} \gamma_{eo}}$$

γ_e and γ_o are internal field constants.

For a single crystal with the known crystals structure it is possible to determine the internal field factors. Because of the change in the order parameter with temperature in liquid crystal the internal field factors are temperature dependent. But since $\gamma_e + 2\gamma_o = 4\pi$ the equation can be written as

$$\frac{1}{\alpha_e} + \frac{2}{\alpha_o} = \frac{4\pi N}{3}\left[\frac{\eta_e^2+2}{\eta_e^2-1} + \frac{2(\eta_o^2+2)}{\eta_o^2-1}\right] \cdots (5$$

In the isotropic phase

$$\gamma_e = \gamma_o = \frac{4\pi}{3}, \quad \eta_e = \eta_o = \eta \text{ and } \alpha_e = \alpha_o = \bar{\alpha}$$

Assumsing that the mean polarizabilites $\bar{\alpha}$ remains the same in all phase, we have

$$\alpha_e + 2\alpha_o = \alpha_{\parallel} + 2\alpha_{\perp} = 3\bar{\alpha} = \frac{9}{4\pi N_i}\left(\frac{\eta^2-1}{\eta^2+2}\right)$$

Where Ni is the number of molecules per cm^3 in the isotropic phase. Using euqation 4 and 5, α_e, α_o are determined by Vuk's and Neugebauer's approaches respectively. The order parameter S can be subsequently calculated from the expression (3).

The values of $\alpha_{\parallel}$ and $\alpha_{\perp}$ ie. the principal molecular polarizabilities parallel and perpendicular to the long axis of the molecules in the crystalline state were obtained by the method of Haller et al.[29] Graphs are plotted for log α_e/α_o vs $\log(T_{NI}$ where T_{NI} is the nematic isotropic transition temperature. These plots are straight lines at low temperatures and intersect the log $\frac{\alpha_e}{\alpha_e}$ axis at Ø degree K., assumed to correspond to log $\frac{\alpha_{\parallel}}{\alpha_{\perp}}$ values in the crystalline state.

The tables 2.2 (a) to 2.2 (o) gives the values of α_e, α_o and S calculated from Vuk's and Neugebauer's models. The results of $\alpha_{\parallel}$ and $\alpha_{\perp}$ obtained graphically are also included in the tables. The temperature variation of the order parameter obtained from both Vuk's and Neugebauer's approaches are shown in the above, figures 2.2 (a) to 2.2 (o) for different liquid crystal samples.

It can be seen from the figures that the order parameter S for the liquid crystals studied are comparable when evaluated from the methods of Neugebauer's and Vuk's. Though the anisotropy of the effective polarizabilities $(\alpha_e - \alpha_o)$ in the nematic phase obtained from the two methods are appreciably different, for example in PCH-7 in the nematic state at 31 degree C the values are 8 $(A^{\circ})^3$ and 1Ø.54 $(A^{\circ})^3$ from Neugebauer's and Vuk's respectively. The reason for similar values of the order parameters from these methods is that the anisotropy of the principal polarizabilites $(\alpha_{\parallel} - \alpha_{\perp})$ increases in the same proportion, when one uses Vuks' or Neugebauer's method. It was shown by Subramanmyam et al[3Ø] that the polarizability values obtained from the Neugebauer's relations agree well with the calculated values of isotropic

Table 2.2 (a)

Temperature variation of effective and mean polarzabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 A° order parameter S of FCH-3

$\tau = \frac{T-T_{ni}}{T_{ni}} \times 10^2$	$\bar{\alpha}$ (A^{o3})	Neugebauer's Method α_o (A^{o3})	α_e (A^{o3})	(S)	Vuk's Method α_o (A^{o3})	α_e (A^{o3})	S
-1.25	28.39	26.66	31.85	0.63	26.31	32.54	0.67
-1.10	28.40	26.69	31.82	0.63	26.35	32.50	0.66
-0.94	28.40	26.75	31.71	0.61	26.41	32.38	0.64
-0.78	28.41	26.76	31.70	0.60	26.43	32.36	0.64
-0.63	28.41	26.83	31.58	0.58	26.51	32.21	0.61
-0.47	28.42	26.86	31.54	0.57	26.55	32.16	0.60
-0.31	28.43	29.91	31.45	0.55	26.61	32.05	0.58
		$\alpha_\perp$ 25.87 (A^{o3})	$\alpha_\parallel$ 34.06 (A^{o3})		$\alpha_\perp$ 25.49 (A^{o3})	$\alpha_\parallel$ 34.82 (A^{o3})	

PCH-3

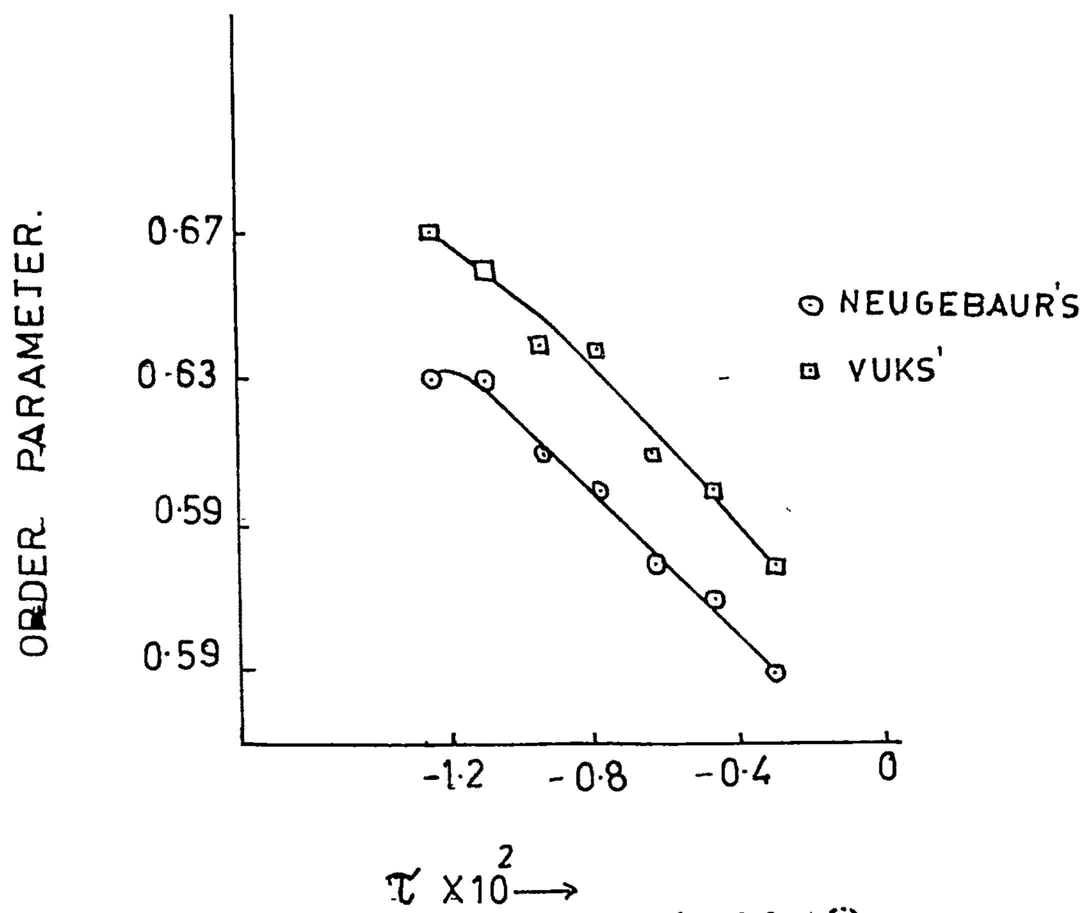


Fig. 2·2·a.(i)

Table 2.2 (b)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of PCH-5

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-7.599	32.26	29.92	36.95	0.65	29.44	37.92	0.63
-6.991	32.27	29.94	36.91	0.65	29.47	37.85	0.62
-6.383	32.24	29.97	36.79	0.63	29.50	37.72	0.61
-5.775	32.23	30.03	36.65	0.61	29.57	37.55	0.59
-5.167	32.24	30.05	36.60	0.61	29.65	37.35	0.57
-4.559	32.23	30.16	36.38	0.58	29.74	37.21	0.56
-3.951	32.23	30.22	36.23	0.56	29.81	37.05	0.54
-3.343	32.24	30.29	36.13	0.55	29.90	36.90	0.52
-2.736	32.23	30.37	35.96	0.52	29.99	36.72	0.50
-2.128	32.25	30.42	35.89	0.51	30.08	36.56	0.48
-1.520	32.27	30.61	35.59	0.46	30.28	36.26	0.44
-0.608	32.21	30.91	35.10	0.39			

	Neugebauer's Method		Vuk's Method	
	$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
	28.81	39.60	27.92	41.38
	(Å^3)	(Å^3)	(Å^3)	(Å^3)

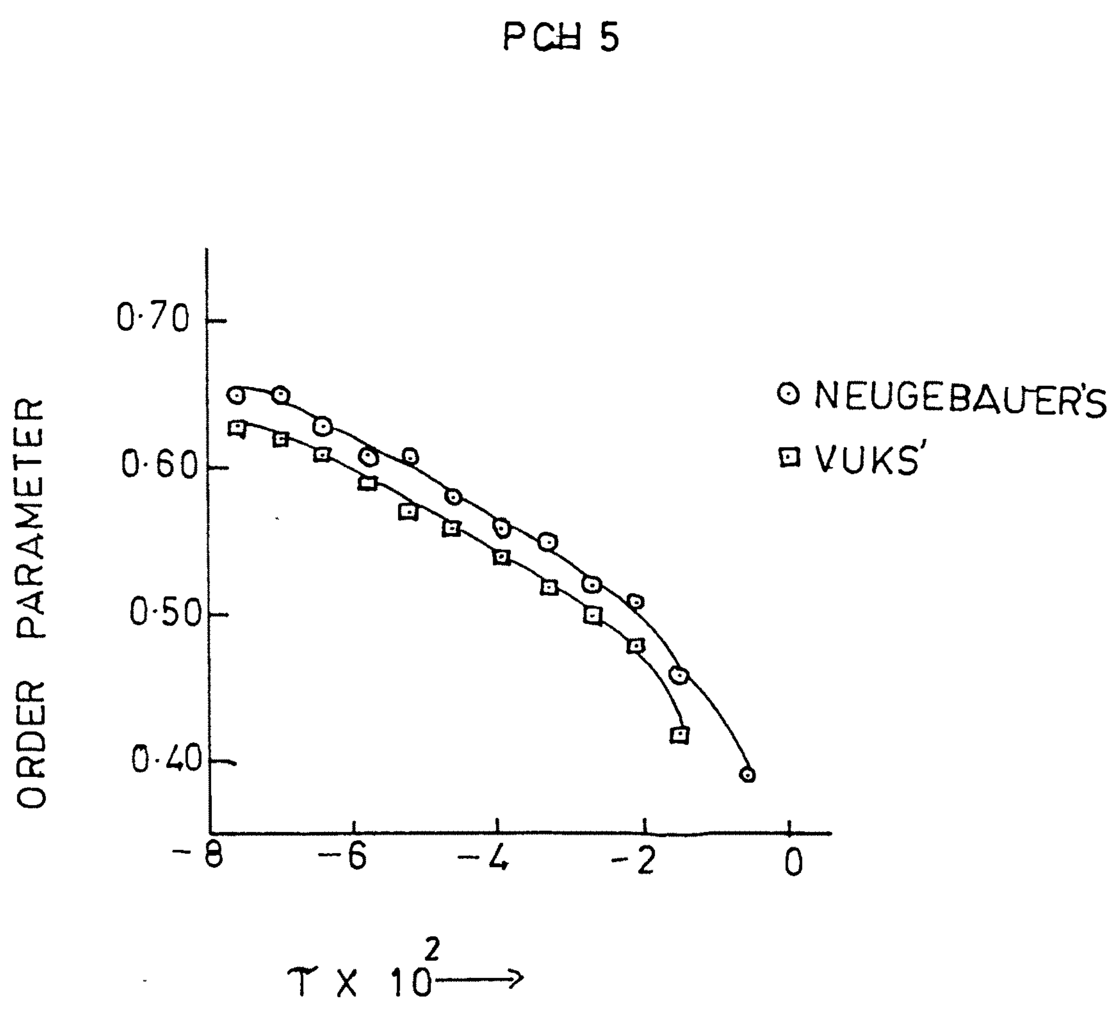

PCH 5
ORDER PARAMETER
0·70
0·60
0·50
0·40
− 8
−6
−4
−2
0
NEUGEBAUER'S
VUKS'
T X 10^2 →

Fig. 2·2 b(i)

Table 2.2 (c)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of FCH-7

		Neugebauer's Method			Vuk's Method		
$\tau = \frac{T-T_{ni}}{T_{ni}} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	(S)	α_o (Å^3)	α_e (Å^3)	S
-8.157	36.68	34.01	42.01	0.58	33.46	43.10	0.60
-7.553	36.64	34.04	41.85	0.57	33.51	42.91	0.59
-6.947	36.66	34.12	41.74	0.55	33.60	42.77	0.57
-6.344	36.65	34.18	41.60	0.54	33.68	42.60	0.56
-6.042	36.66	34.23	41.51	0.53	33.74	42.48	0.55
-5.740	36.65	34.34	41.26	0.50	33.80	42.35	0.53
-5.136	36.64	34.34	41.24	0.50	33.87	42.19	0.52
4.532	36.64	34.40	41.12	0.49	33.95	42.03	0.50
3.927	36.65	34.49	40.97	0.47	34.05	41.87	0.49
3.323	36.65	34.56	40.83	0.46	34.15	41.63	0.47
2.719	36.65	34.66	40.63	0.43	34.43	41.45	0.44
2.115	36.65	34.77	40.40	0.41	34.39	41.17	0.42
1.511	36.70	34.93	40.23	0.39	34.57	40.96	0.40
0.906	36.87	35.26	40.08	0.35	34.94	40.72	0.36
		$\alpha_\perp$ 32.36 (Å^3)	$\alpha_\parallel$ 46.14 (Å^3)		$\alpha_\perp$ 31.62 (Å^3)	$\alpha_\parallel$ 47.64 (Å^3)	

PCH 7

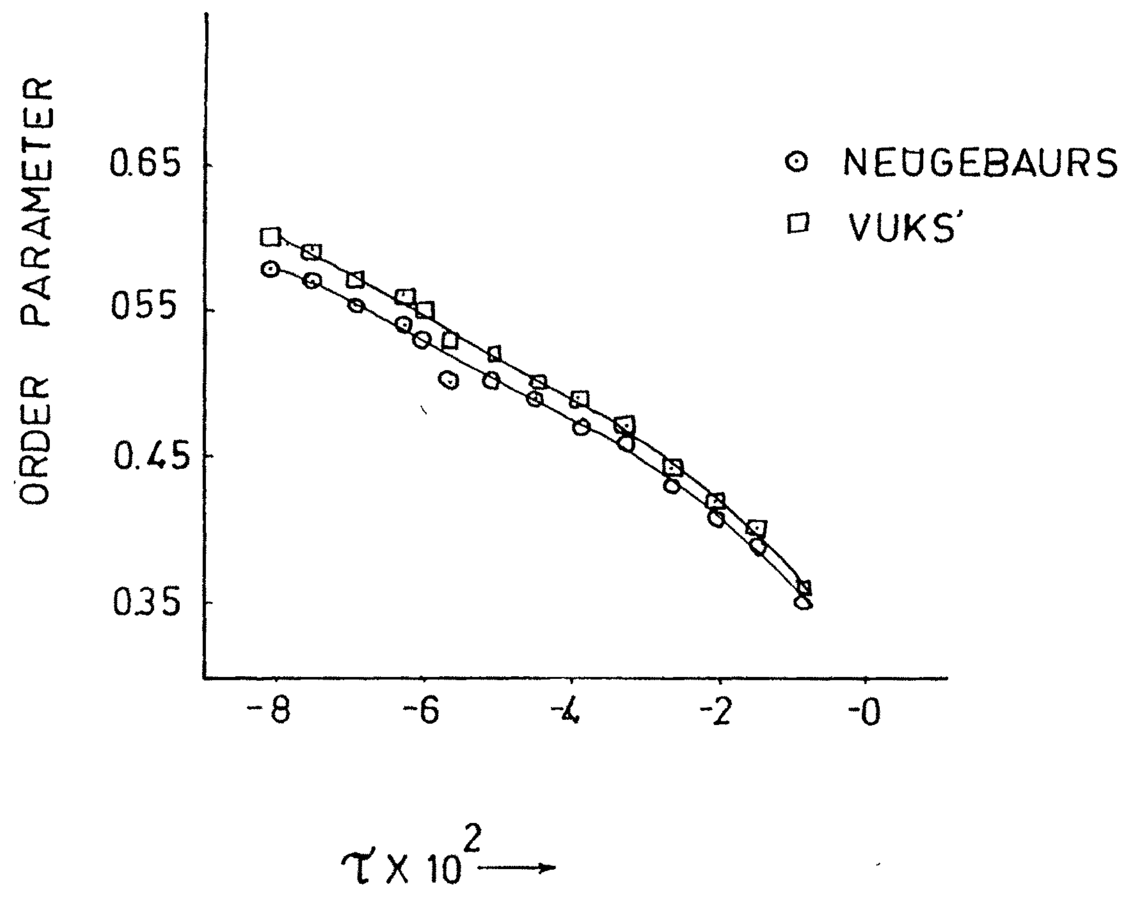


Fig 2.2 c (i)

Table 2.2 (d)

Temperature variation of effective and mean polarizabilities α_ℓ, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of D-302

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_ℓ (Å^3)	S	α_o (Å^3)	α_ℓ (Å^3)	S
-7.955	33.17	31.48	36.55	0.75	31.16	37.17	0.75
-6.960	33.17	31.54	36.43	0.72	31.24	37.04	0.72
-6.25	33.18	31.56	36.41	0.71	31.26	37.01	0.71
-5.398	33.20	31.60	36.40	0.71	31.30	36.99	0.71
-4.545	33.21	31.66	36.30	0.69	31.37	36.88	0.69
-3.693	33.22	31.72	36.22	0.66	31.44	36.76	0.66
-2.841	33.23	31.81	36.06	0.63	31.56	36.57	0.62
-1.989	33.26	31.89	35.98	0.61	31.64	36.48	0.60
-1.136	33.27	32.01	35.79	0.56	31.78	36.26	0.56
-0.568	33.30	32.16	35.56	0.50	31.88	36.16	0.53
-0.284	33.31	32.27	35.40	0.46	32.08	35.78	0.46
		$\alpha_\perp$ 31.16 (Å^3)	$\alpha_\parallel$ 37.94 (Å^3)		$\alpha_\perp$ 30.74 (Å^3)	$\alpha_\parallel$ 38.79 (Å^3)	

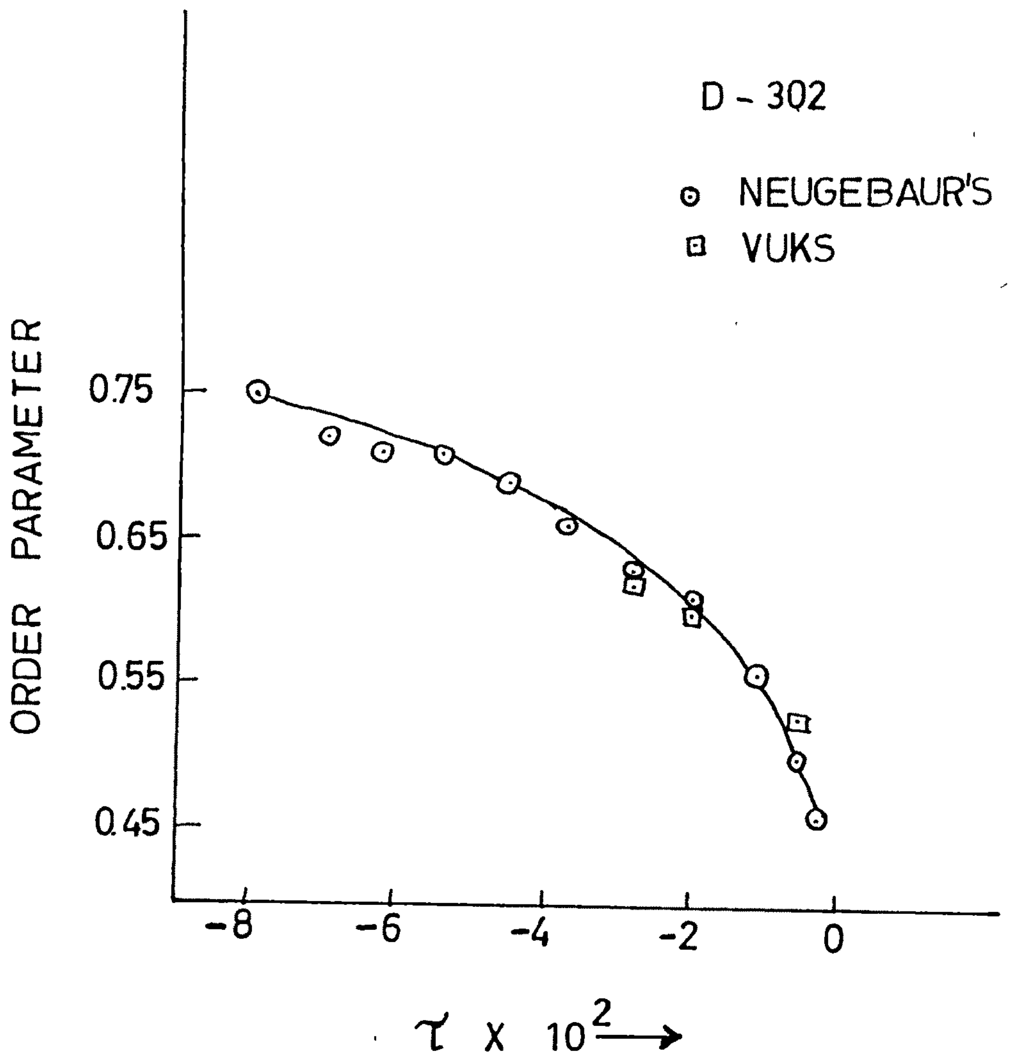

D - 3Q2
NEUGEBAUR'S
VUKS
ORDER PARAMETER
0.75
0.65
0.55
0.45
-8
-6
-4
-2
0
τ x 10²

fig 2.2d (i)

Table 2.2 (e)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å and order parameter S of D - 402

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ ($Å^3$)	α_o ($Å^3$)	α_e ($Å^3$)	S	α_o ($Å^3$)	α_e ($Å^3$)	S
-10.187	35.03	33.18	38.74	0.73	32.83	39.43	0.73
-9.039	35.04	33.26	38.62	0.70	32.92	39.27	0.70
-8.608	35.04	33.22	38.68	0.71	32.88	39.36	0.72
-6.743	35.05	33.35	38.46	0.67	33.03	39.07	0.67
-5.739	35.05	33.40	38.35	0.65	33.09	38.97	0.65
-4.591	35.04	33.45	38.22	0.62	33.15	38.82	0.63
-3.300	35.04	33.56	38.00	0.58	33.30	38.51	0.57
-2.439	35.05	33.66	37.85	0.55	33.40	38.36	0.55
-1.865	35.06	33.72	37.75	0.53	33.46	38.26	0.53
1.291	35.08	33.77	37.68	0.51	33.55	38.12	0.50
0.717	35.09	33.91	37.46	0.46	33.72	37.84	0.45
0.430	35.10	34.02	37.27	0.42	33.52	37.64	0.45

	$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
	32.58 ($Å^3$)	40.22 ($Å^3$)	32.10 ($Å^3$)	41.17 ($Å^3$)

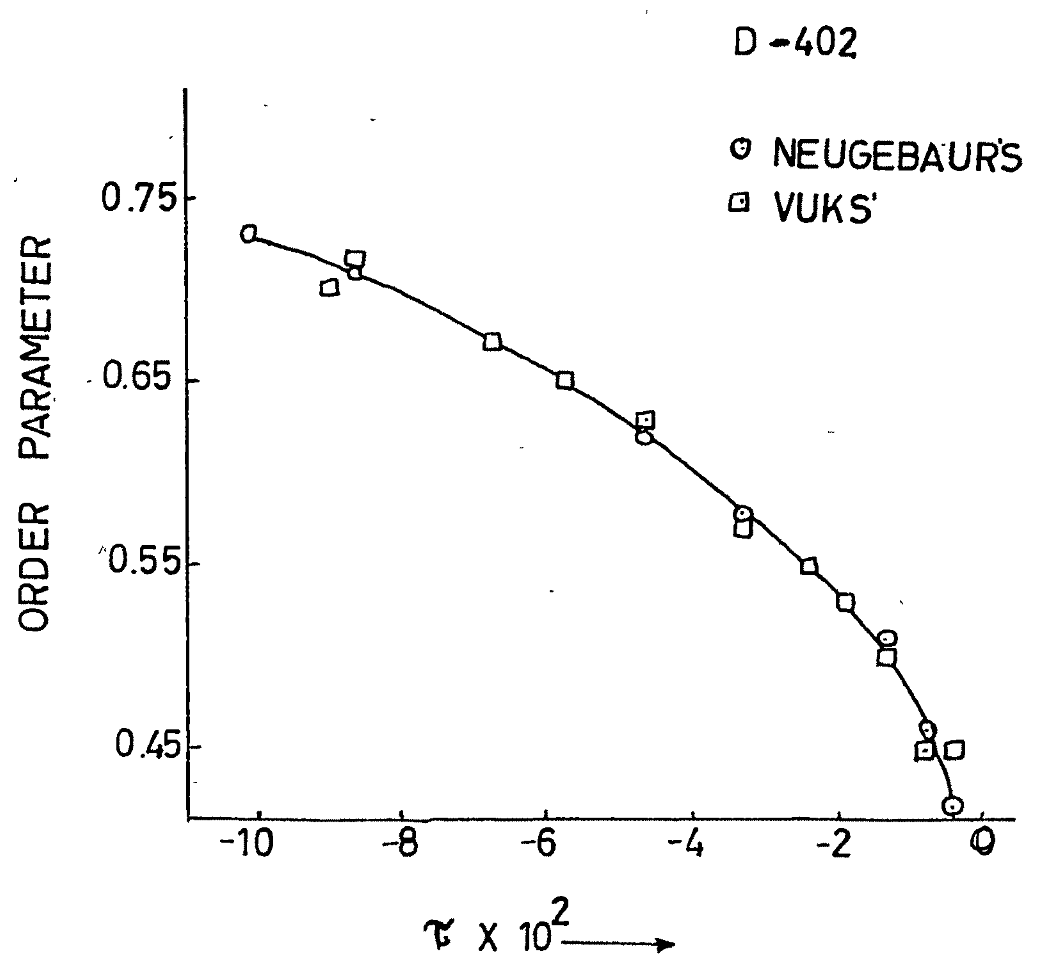

D -402
NEUGEBAUR'S
VUKS'
ORDER PARAMETER
0.75
0.65
0.55
0.45
-10
-8
-6
-4
-2
0
τ X 10²

Table 2.2 (A)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for $\lambda = 5890$ Å order parameter S of D - 501

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-9.928	34.87	33.27	38.07	0.73	32.98	38.65	0.73
-7.050	34.90	33.36	37.99	0.71	33.07	38.56	0.71
-4.029	34.72	33.35	37.45	0.63	33.08	37.99	0.63
-2.734	34.96	33.67	37.54	0.59	33.43	38.01	0.59
-1.295	35.00	33.92	37.15	0.49	33.71	37.57	0.50
-0.576	35.03	34.19	36.73	0.39	34.00	37.11	0.40

$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
32.94	39.48	32.53	40.28
(Å^3)	(Å^3)	(Å^3)	(Å^3)

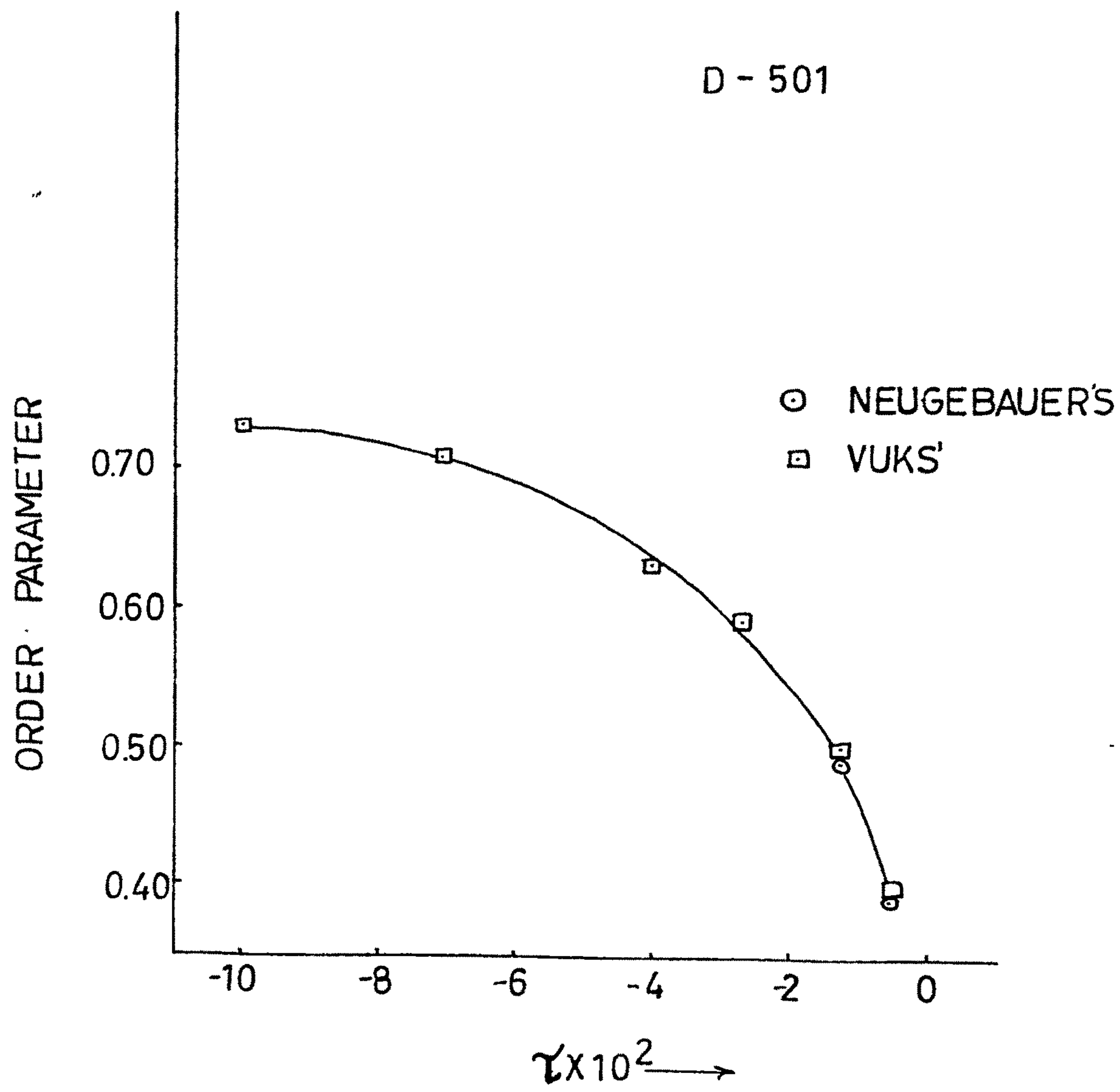

D - 501
NEUGEBAUER'S
VUKS'
ORDER · PARAMETER
0.70
0.60
0.50
0.40
-10
-8
-6
-4
-2
0
τ X 10^2

Fig 2.2.4 (i)

Table 2.2 g

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ= 5890 Å order parameter S of D - 55

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-3.438	41.62	39.99	44.91	0.69	39.68	45.53	0.70
-3.125	41.62	39.99	44.90	0.69	39.66	45.55	0.70
-2.500	41.62	40.06	44.75	0.66	39.76	45.36	0.67
-1.875	41.63	40.09	44.71	0.65	39.82	45.24	0.65
-1.250	41.64	40.20	44.52	0.60	39.87	45.02	0.61
-0.625	41.65	40.41	44.13	0.52	40.19	44.57	0.52

$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
31.31	46.40	38.87	47.27
(Å^3)	(Å^3)	(Å^3)	(Å^3)

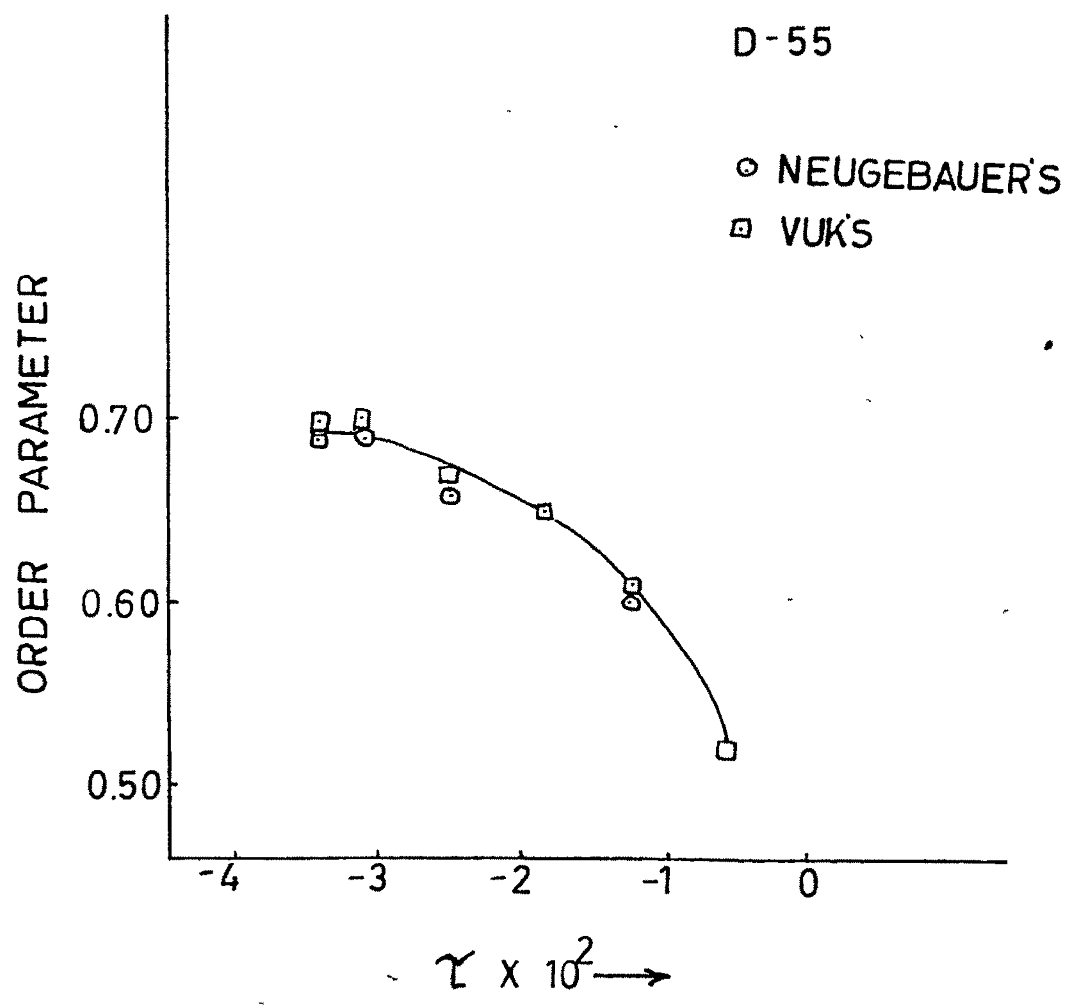

D-55
NEUGEBAUER'S
VUK'S
ORDER PARAMETER
0.70
0.60
0.50
-4
-3
-2
-1
0
τ x 10²

Table 2.2 (h)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 A° and order parameter S of CPBB

		Neugebauer's Method			Vuk's Method		
$=(T-T_{NI})/T_{NI}$ $\times 10^2$	$\bar{\alpha}$ $(A^{\circ})^3$	α_o $(A^{\circ})^3$	α_e $(A^{\circ})^3$	S	α_o $A^{\circ 3}$	α_e $A^{\circ 3}$	S
-0.633	32.81	30.81	36.82	0.49	30.40	37.61	0.48
-0.949	32.82	30.70	37.07	0.52	30.23	38.01	0.52
-1.266	32.82	30.58	37.31	0.55	30.08	38.29	0.55
-1.582	32.80	30.48	37.44	0.56	29.97	38.47	0.57
-1.899	32.79	30.40	37.57	0.58	29.88	38.62	0.59
-2.215	32.78	30.32	37.69	0.60	29.79	38.77	0.60
-2.532	32.78	30.26	37.82	0.61	29.69	38.94	0.62

	Neugebauer's Method		Vuk's Method	
	$\alpha_{\perp}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha_{\parallel}$
	28.81	41.17	27.96	42.86
	$(A^{\circ})^3$	$(A^{\circ})^3$	$(A^{\circ})^3$	$(A^{\circ})^3$

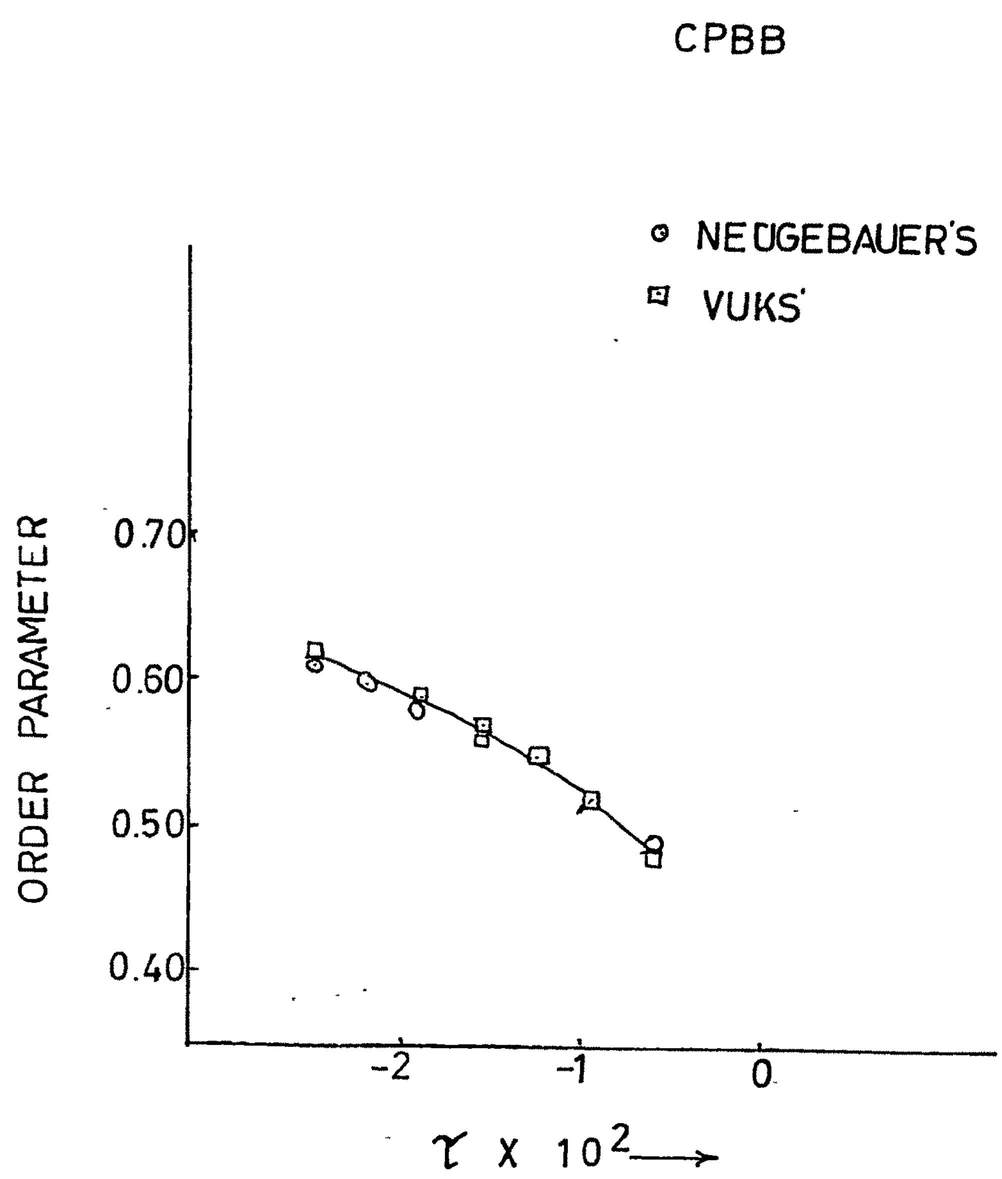

CPBB
NEUGEBAUER'S
VUKS'
ORDER PARAMETER
0.70
0.60
0.50
0.40
-2
-1
0
τ X 10^2 →

FIG. 2.2h (i).

Table 2.2 (i)

Temperature variation of effective and mean polarzabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å
A order parameter S of CFFOB

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-1.560	36.09	33.42	41.42	0.49	33.04	42.17	.47
-2.128	35.89	33.24	41.18	0.49	32.67	42.32	.50
-2.979	35.86	33.05	41.49	0.52	32.38	42.82	.55
-3.972	35.89	32.80	42.06	0.57	32.13	43.39	.59
-4.823	35.82	32.69	42.09	0.58	32.00	43.47	.60
-5.816	35.82	32.55	42.36	0.61	31.84	43.79	.63
-6.809	35.76	32.42	42.43	0.62	31.68	43.91	.65
-7.660	35.71	32.27	42.60	0.64	31.50	44.14	.66
-8.652	35.70	32.11	42.87	0.67	31.32	44.46	.69
		$\alpha_\perp$	$\alpha_\parallel$		$\alpha_\perp$	$\alpha_\parallel$	
		30.66 (Å^3)	46.84 (Å^3)		29.68 (Å^3)	48.80 (Å^3)	

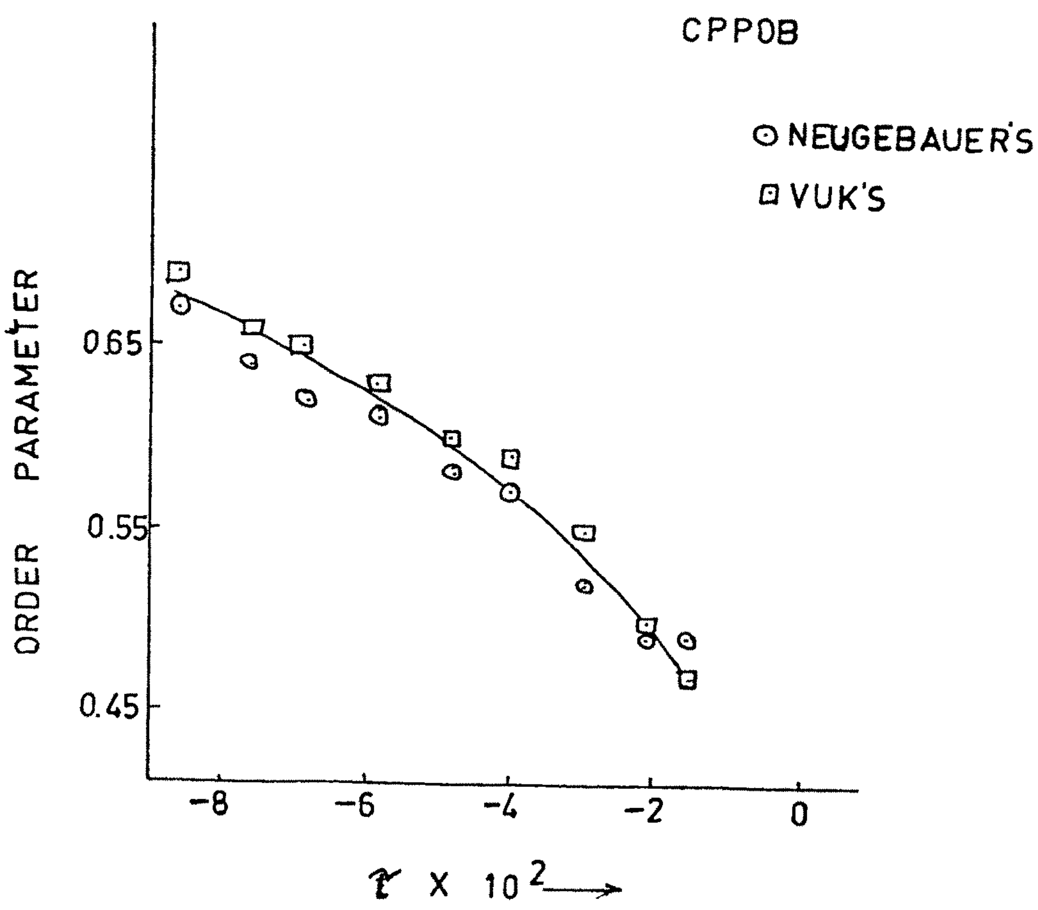

CPPOB
NEUGEBAUER'S
VUK'S
ORDER PARAMETER
0.65
0.55
0.45
-8
-6
-4
-2
0
τ X 10²

fig 2·2 i(i)

Table 2.2 j

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of E -4

		Neugebauer's Method			Vuks's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-7.164	36.58	32.68	44.37	0.64	31.78	46.18	0.65
-5.672	36.61	32.91	44.00	0.61	32.07	45.69	0.62
-4.478	36.63	33.09	43.71	0.59	32.28	45.32	0.59
-3.582	36.64	33.25	43.41	0.56	32.49	44.93	0.56
-2.687	36.68	33.42	43.19	0.54	32.68	44.66	0.54
-1.791	36.71	33.69	42.75	0.51	33.01	44.09	0.50
-0.896	36.71	34.07	41.99	0.44	33.48	43.16	0.44

	Neugebauer's Method		Vuks's Method	
	$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
	30.82	48.95	29.49	51.61
	(Å^3)	(Å^3)	(Å^3)	(Å^3)

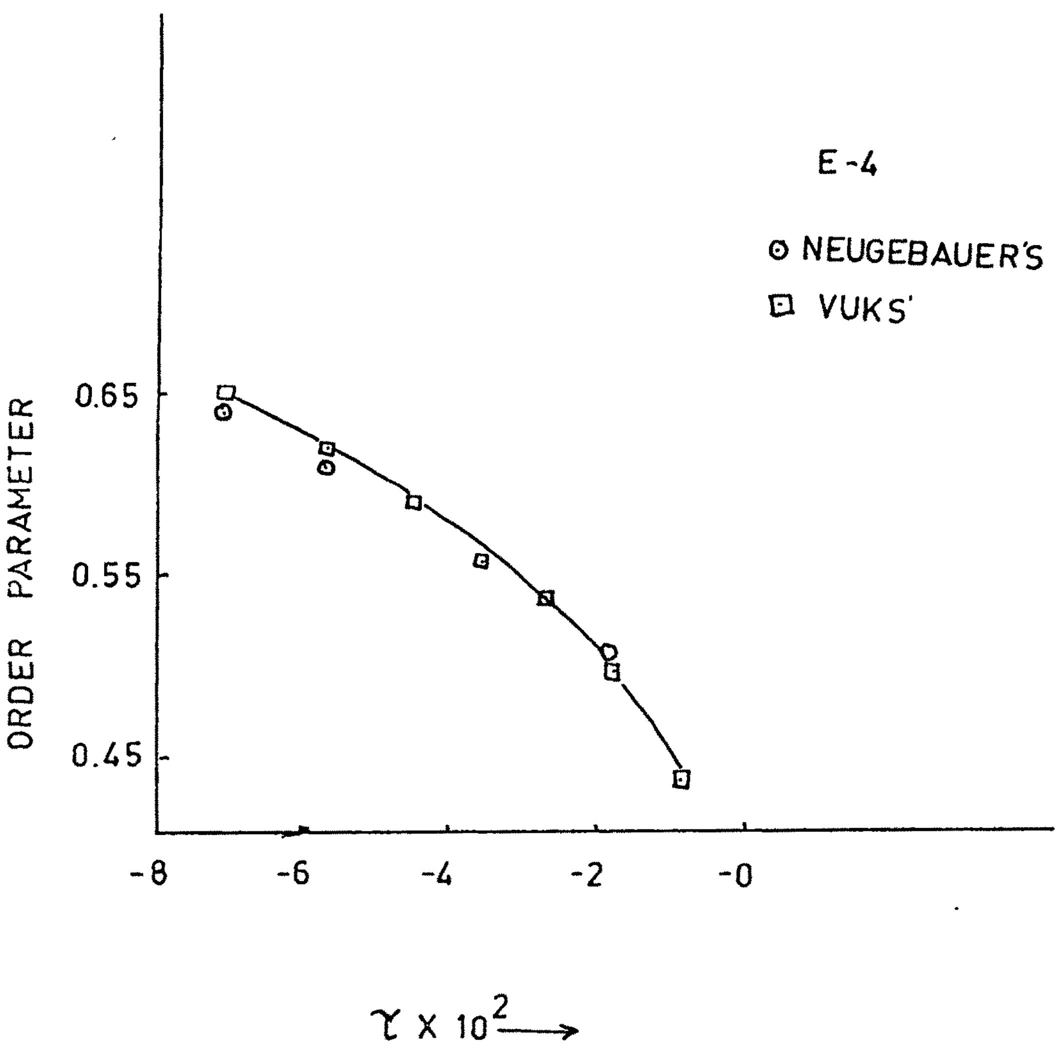

E-4
NEUGEBAUER'S
VUKS'
ORDER PARAMETER
0.65
0.55
0.45
-8
-6
-4
-2
-0
τ X 10²

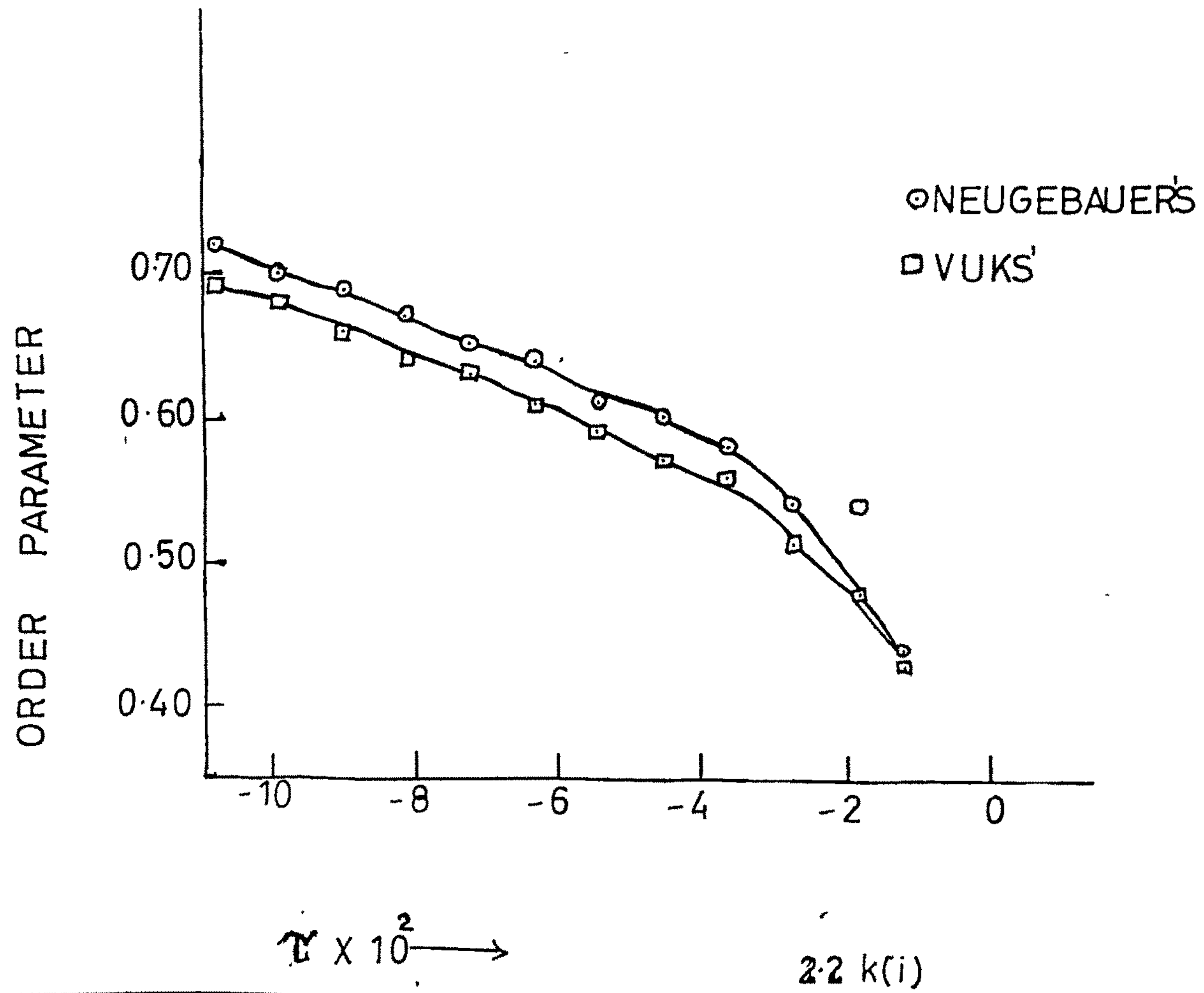
fig. 2.2 j(i)

Table 2.2 (k)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for $\lambda = 5890$ Å
order parameter S of E -7

		Neugebauer's Method			Vuk's Method		
$\tau = \frac{T - T_{NI}}{T_{NI}} \times 10^{2}$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	(S)	α_o (Å^3)	α_e (Å^3)	S
-10.811	35.56	31.48	43.71	0.72	30.51	45.66	0.69
-9.910	35.58	31.58	43.59	0.70	30.63	45.51	0.68
-9.009	35.59	31.68	43.42	0.69	30.76	45.27	0.66
-8.108	35.61	31.81	43.20	0.67	30.91	45.01	0.64
-7.207	35.65	31.92	43.10	0.65	31.04	44.84	0.63
-6.306	35.66	32.04	42.90	0.64	31.19	44.59	0.61
5.405	35.67	32.21	42.59	0.61	31.40	44.22	0.59
4.505	35.72	32.32	42.53	0.60	31.53	44.12	0.57
3.604	35.80	32.50	42.41	0.58	31.73	43.96	0.56
2.703	35.80	32.71	41.99	0.54	31.99	43.43	0.52
1.802	35.85	33.02	41.50	0.54	32.37	42.80	0.48
1.201	35.87	33.35	40.90	0.44	32.75	42.10	0.43
		$\alpha_\perp$	$\alpha_\parallel$		$\alpha_\perp$	$\alpha_\parallel$	
		30.34 (Å^3)	47.43 (Å^3)		28.74 (Å^3)	50.63 (Å^3)	

E-7


ORDER PARAMETER
0·70
0·60
0·50
0·40
-10
-8
-6
-4
-2
0
⊙ NEUGEBAUER'S
□ VUKS'
τ X 10² →

2·2 k(i)

Table 2.2 (1)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of CCH

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-0.932	26.48	25.90	27.65	0.65	25.82	27.81	0.62
-0.776	26.50	25.92	27.65	0.64	25.85	27.79	0.60
-0.621	26.50	25.95	27.61	0.62	25.88	27.74	0.58
-0.466	26.51	25.97	27.59	0.60	25.90	27.71	0.56
-0.311	26.52	26.03	27.50	0.55	25.96	27.64	0.52
		$\alpha_\perp$	$\alpha_\parallel$		$\alpha_\perp$	$\alpha_\parallel$	
		25.70 (Å^3)	28.38 (Å^3)		25.53 (Å^3)	28.73 (Å^3)	

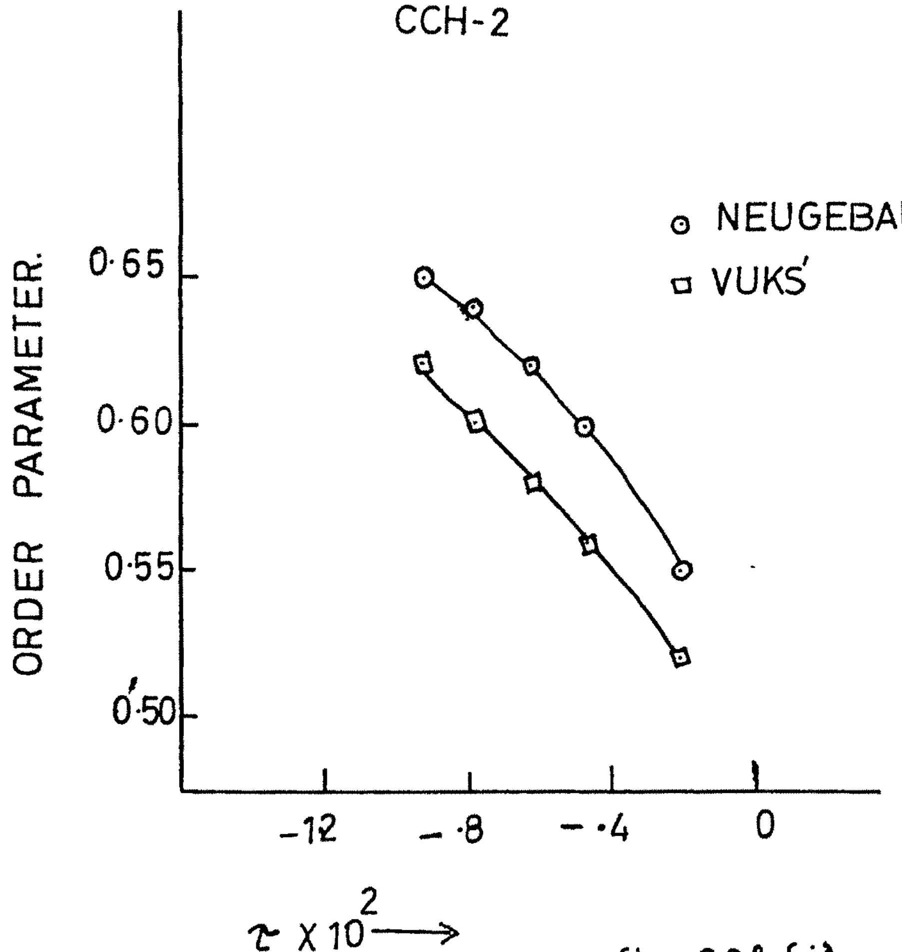

CCH-2
NEUGEBAUER'S
VUKS'
ORDER PARAMETER.
0·65
0·60
0·55
0·50
-12
-·8
-·4
0
τ X 10^2 →

fig. 2·2l (i)

Table 2.2 (a)

Temperature variation of effective and mean polarizabilities α_e, α_o and $\bar{\alpha}$ for $\lambda = 5890$ Å and order parameter S of CCH - 3.

		Neugebauer's Method			Vuk's Method		
$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_o (Å^3)	α_e (Å^3)	S	α_o (Å^3)	α_e (Å^3)	S
-6.751	28.42	27.48	30.29	0.66	27.30	30.64	0.65
-5.767	28.41	27.49	30.24	0.64	27.33	30.57	0.63
-5.204	28.43	27.53	30.24	0.63	27.38	30.54	0.61
-4.501	28.42	27.56	30.15	0.61	27.40	30.46	0.59
-3.938	28.43	27.60	30.09	0.58	27.45	30.38	0.56
-3.376	28.44	27.62	30.08	0.57	27.50	30.32	0.54
-2.672	28.45	27.67	30.02	0.55	27.54	30.28	0.53
-1.828	28.45	27.73	29.90	0.51	27.59	30.17	0.50
-1.266	28.47	27.78	29.85	0.49	27.66	30.08	0.47
-0.563	28.47	27.87	29.66	0.42	27.76	29.86	0.40
		$\alpha_\perp$	$\alpha_\parallel$		$\alpha_\perp$	$\alpha_\parallel$	
		26.91	30.09		27.21	31.49	
		(Å^3)	(Å^3)		(Å^3)	(Å^3)	

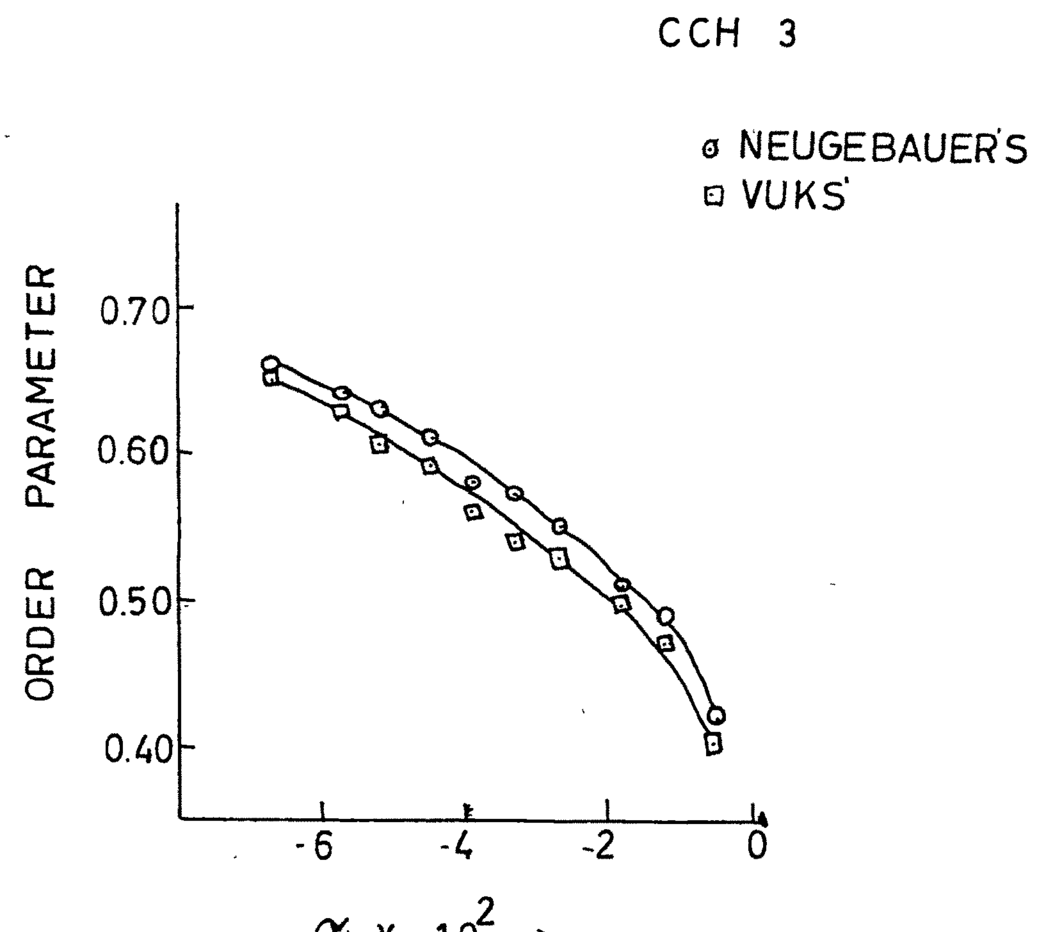

CCH 3
NEUGEBAUER'S
VUKS'
ORDER PARAMETER
0.70
0.60
0.50
0.40
-6
-4
-2
0
τ x 10^2

fig. 2.2 m(i)

Table 2.2 (n)

Temperature variation of effective and mean polarzabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of CCH - 5.

$\tau = (T-T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	Neugebauer's Method α_e (Å^3)	α_o (Å^3)	S	Vuk's Method α_e (Å^3)	α_o (Å^3)	S
-5.587	32.17	31.05	34.42	0.61	30.84	34.85	0.61
-4.749	32.18	31.02	34.51	0.64	30.80	34.96	0.64
-3.631	32.2	31.08	34.44	0.61	30.86	34.88	0.62
-2.514	32.22	31.15	34.35	0.58	30.96	34.73	0.58
-1.955	32.22	31.22	34.23	0.55	31.05	34.58	0.56
-1.117	32.24	31.40	33.92	0.46	31.23	34.26	0.46
-0.559	32.25	31.51	33.73	0.41	31.38	34.00	0.40

	Neugebauer's Method $\alpha_\perp$	Neugebauer's Method $\alpha_\parallel$	Vuk's Method $\alpha_\perp$	Vuk's Method $\alpha_\parallel$
	30.67 (Å^3)	36.16 (Å^3)	30.32 (Å^3)	36.85 (Å^3)

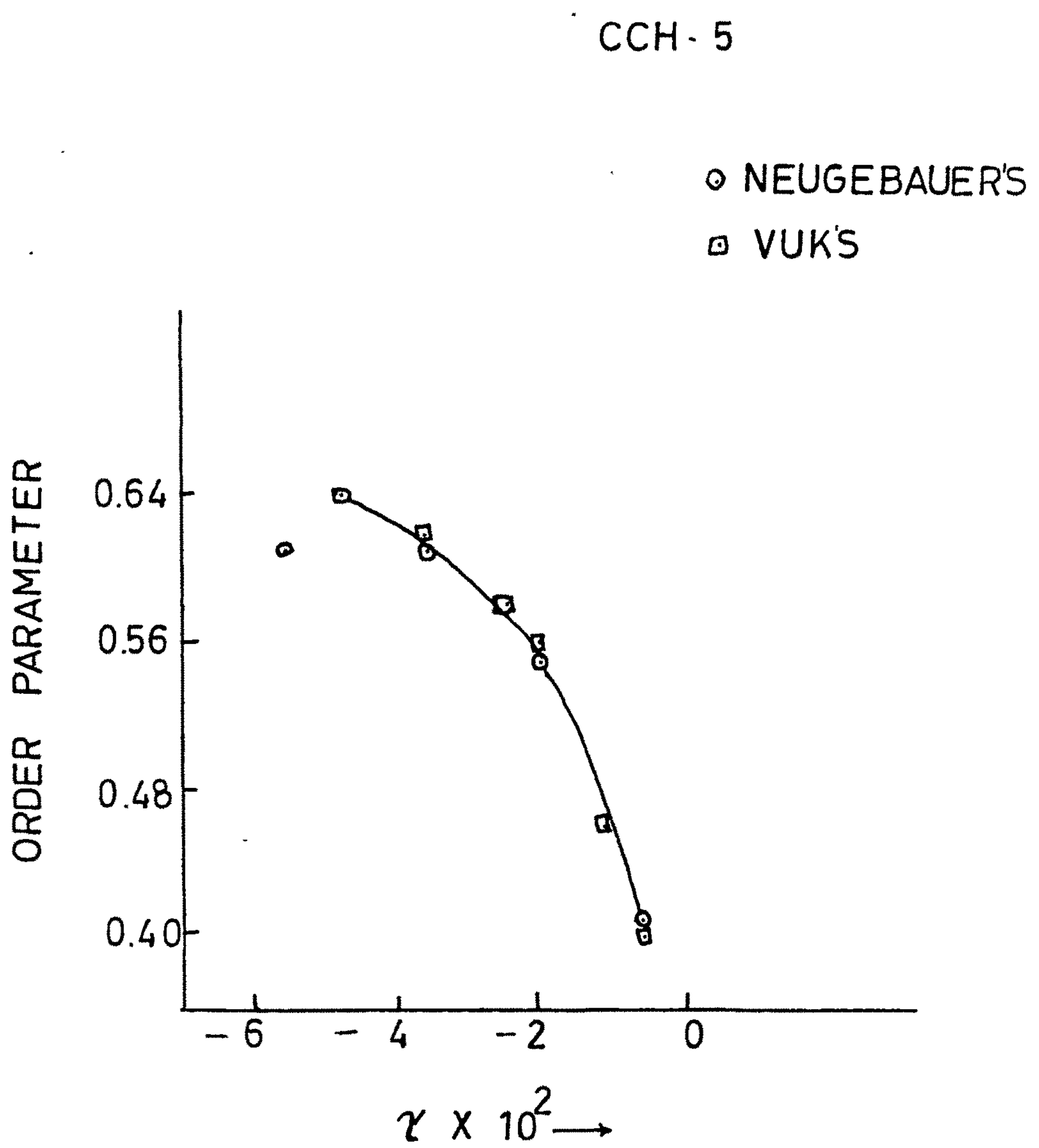

CCH - 5
NEUGEBAUER'S
VUK'S
ORDER PARAMETER
0.64
0.56
0.48
0.40
- 6
- 4
- 2
0
τ X 10²

fig. 2.2 n (i).

Table 2.2 (a)

Temperature variation of effective and mean polarzabilities α_e, α_o and $\bar{\alpha}$ for λ = 5890 Å order parameter S of CCH − 7.

		Neugebauer's Method			Vuk's Method		
$\tau = (T - T_{NI})/T_{NI} \times 10^2$	$\bar{\alpha}$ (Å^3)	α_e Å^3	α_o (Å^3)	S	α_e Å^3	α_o Å^3	S
-3.641	35.86	34.71	38.16	0.54	34.49	38.60	0.52
-3.361	35.85	34.72	38.10	0.53	34.50	38.54	0.51
-3.081	35.84	34.75	38.03	0.52	34.54	38.45	0.49
-2.801	35.84	34.76	38.01	0.51	34.57	38.37	0.48
-2.521	35.84	34.79	37.95	0.50	34.61	38.30	0.47
-2.241	35.84	34.85	37.82	0.47	34.65	38.22	0.45
-1.961	35.82	34.86	37.75	0.45	34.68	38.11	0.43
-1.681	35.82	34.89	37.69	0.44	34.72	38.10	0.43
-1.401	35.84	34.92	37.69	0.44	34.76	37.99	0.40
-1.120	35.84	34.96	37.61	0.42	34.81	37.90	0.39
-0.840	35.85	35.00	37.55	0.40	34.86	37.83	0.37

	Neugebauer's Method		Vuk's Method	
	$\alpha_\perp$	$\alpha_\parallel$	$\alpha_\perp$	$\alpha_\parallel$
	33.83 (Å^3)	40.18 (Å^3)	33.31 (Å^3)	41.23 (Å^3)

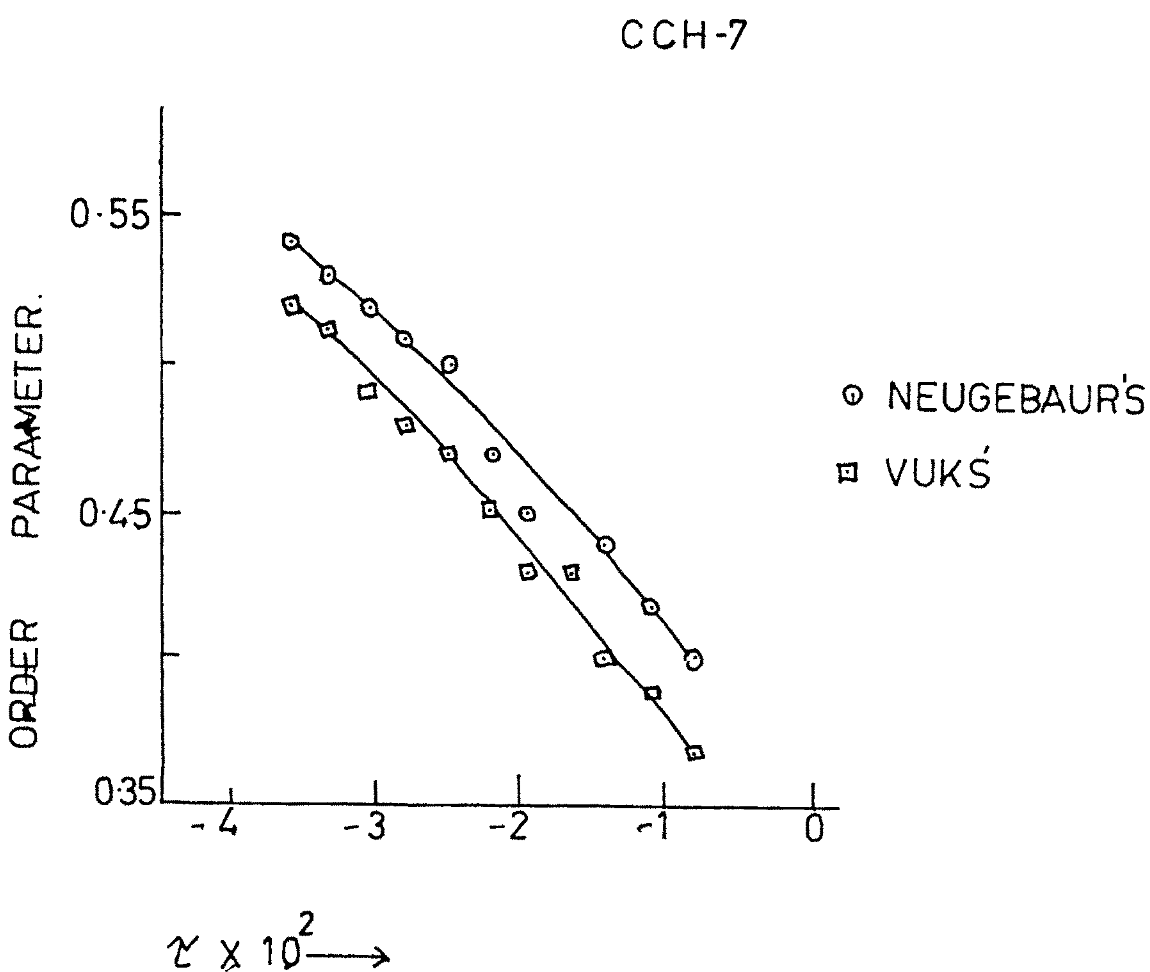

CCH-7
ORDER PARAMETER.
0·55
0·45
0·35
-4
-3
-2
-1
0
⊙ NEUGEBAUR'S
⊡ VUKS'
τ X 10² ⟶

fig 2·2 0(i)

polarizabilities calculated from the bond polarizability data. Moreover the assumptions of anisotropic internal field constants in liquid crystals by Neugebauer's are logical. Vuk's assumed an isotropic internal field in liquid crystalline media, but it is difficult to visualise how in a medium of anisotropic molecular distribution as in liquid crystals the local field would be isotropic. In an anisotropic molecular distribution as in liquid crystals the internal field parameters cannot be the same along the long molecular axis and perpendicular to it. Though the determination of the order parameter of liquid crystals by Neugebauer's and Vuk's methods give nearly the same value, Neugebauer's method is to be prefered as it is theoretically sound in having internal field constants different along and perpendicular to molecular axis. Also the principal polarizabilites obtained by it agree to the values of isotropic polarizabilities obtained from bond polarizability calculations. The S - value decreases gradually with increase of temperature upto the clearing temperature then it suddenly vanishes.

The order parameter for PCH - 7 obtained in the present investigation by the method of refractive index agrees well with that obtained from diamagnetic susceptibility reported earlier.[31]

It can be seen that the order parameter of PCH-5 and PCH -7 at any reduced temperature $\tau = \frac{T - T_{NI}}{T_{NI}}$ is less than the S value of the corresponding pentyl and heptyl cyanobiphenyl at the same reduced temperature.[25,32] It is therefore concluded that the replacement of a phenyl ring in cyanobiphenyls by a cyclohexyl ring reduces the order parameter appreciably.

Recently Mitra et al[33] has reported the order parameter for the samples D 5Ø1 and D 4Ø2 by the method of diamagnetic susceptibility. They are found to be comparable with the values obtained here. The order parameter of D 5Ø1 and D 4Ø2 at say 44 degree C obtained in the present investigation is slightly higher (~Ø.71) than the S value (~Ø.61) reported in the literature. The order parameter of D - 55 and D 3Ø2 has not been reported so far.

Order parameter studies on monotropic liquid crystals samples are also very scarce.

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