

CHAPTER IV

SURFACE TENSION OF NEMATIC LIQUID CRYSTALS

The results of the surface tension studies on five **nematogenic** compounds are presented in this chapter. The substances studied are:

- 1 **p-Azoxyanisole (PAA)**
- 2 **p-Azoxyphenetole (PAP)**
- 3 **Anisaldazine**
- 4 **4-Methoxybenzylidene-4'-butylaniline (MBBA)**
- 5 **4'-n-Pentyl-4-cyanobiphenyl (5CB).**

The first four compounds were obtained from **Eastman Kodak Co.** whereas **5CB** was synthesized in our laboratory. The first three compounds were recrystallised several times from suitable solvents till no **further** improvement in the nematic-isotropic (N-I) transition temperatures were observed. The other two compounds were purified by vacuum sublimation as they are room temperature nematic liquid **crystala**. The transition points of the compounds were determined by a polarizing microscope equipped with a **Mettler FP5** hot stage.

For each compound the surface tension measurements were repeated several times using fresh samples and it was found that the results were quite reproducible. We shall now discuss the results for each substance individually.

PAA

This is perhaps the most widely studied liquid crystal. Its structural formula is given in fig.4.1. The N-I transition temperature of the sample used was 135.2°C. The values of γ were calculated using the density (ρ) data reported by Porter and Johnson.' The values of γ and ρ at different temperatures are given in tables 4.1 and 4.2. Experiments were repeated three times with fresh samples. The agreement in the values from the different experiments was within about 1%.

The γ -T characteristic for this compound is given in fig.4.2. It can be seen that initially

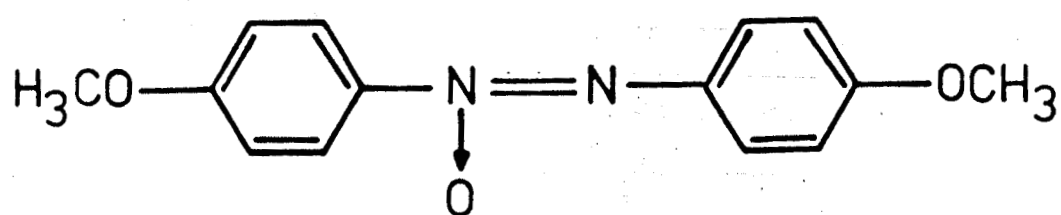


Figure 4.1

Structural formula of p-azoxyanisole

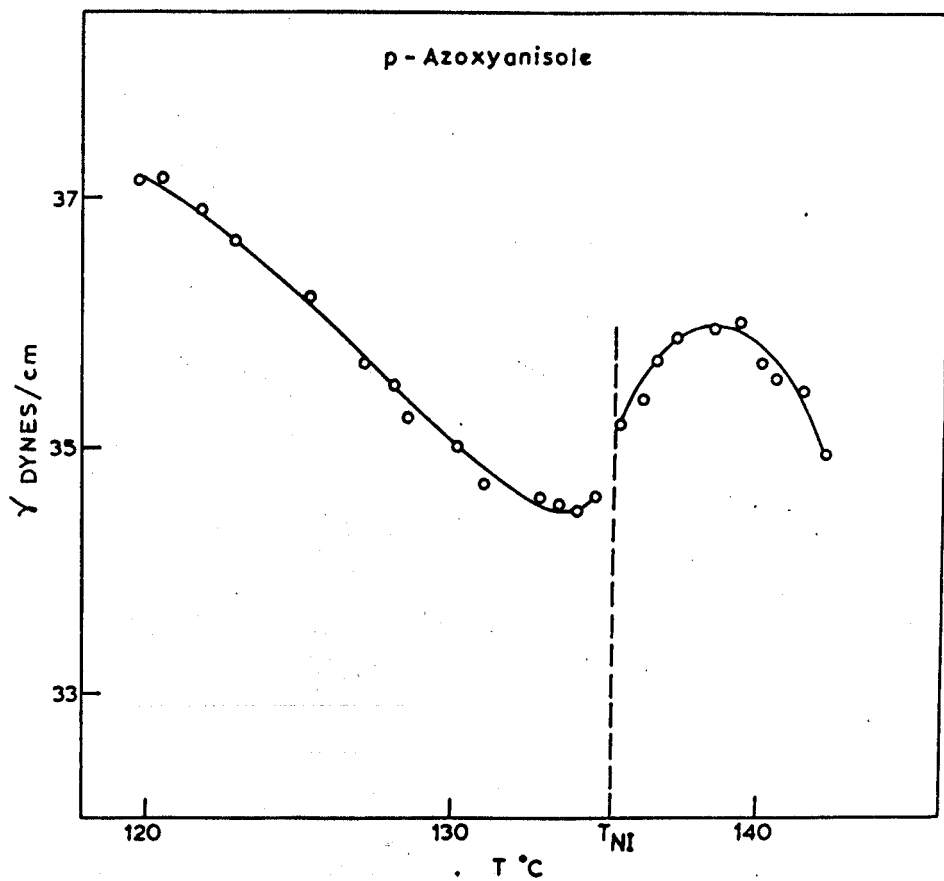


Figure 4.2

Surface **tension**-temperature characteristic **curve** for PAA. (**P**resent investigations)

γ decreases in the nematic phase. As T_{NI} is approached the slope of the γ - T curve becomes positive. At the transition point, there appears to be a discontinuity in the value of γ with a higher value in the isotropic phase. The slope continues to be positive for a few degrees in the isotropic phase after which it changes sign with γ assuming again a monotonic decreasing trend.

The γ - T curves obtained for this compound by earlier workers²⁻⁵ are given in fig.4.3 & 4.4 for comparison. We can see that there is a similarity between our curve and that of Ferguson and Kennedy. Jaegers curve also agrees with our curve to a certain extent though it has only few points along the increasing part of the curve. Another recent determination of the γ - T characteristic of this compound is by Brown and Mann,^{5a} who used the light scattering technique. The γ - T curve obtained by them is also in close agreement with our curve.

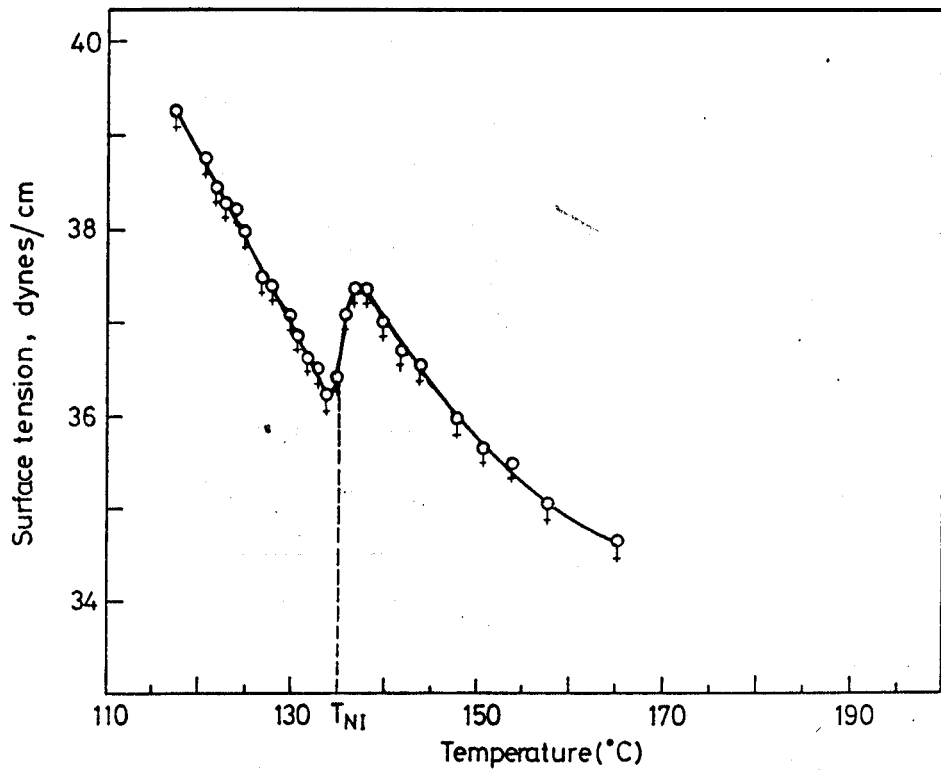


Fig. 4.3 : Surface tension-temperature characteristic curve for PAA (After Ferguson and Kennedy³)

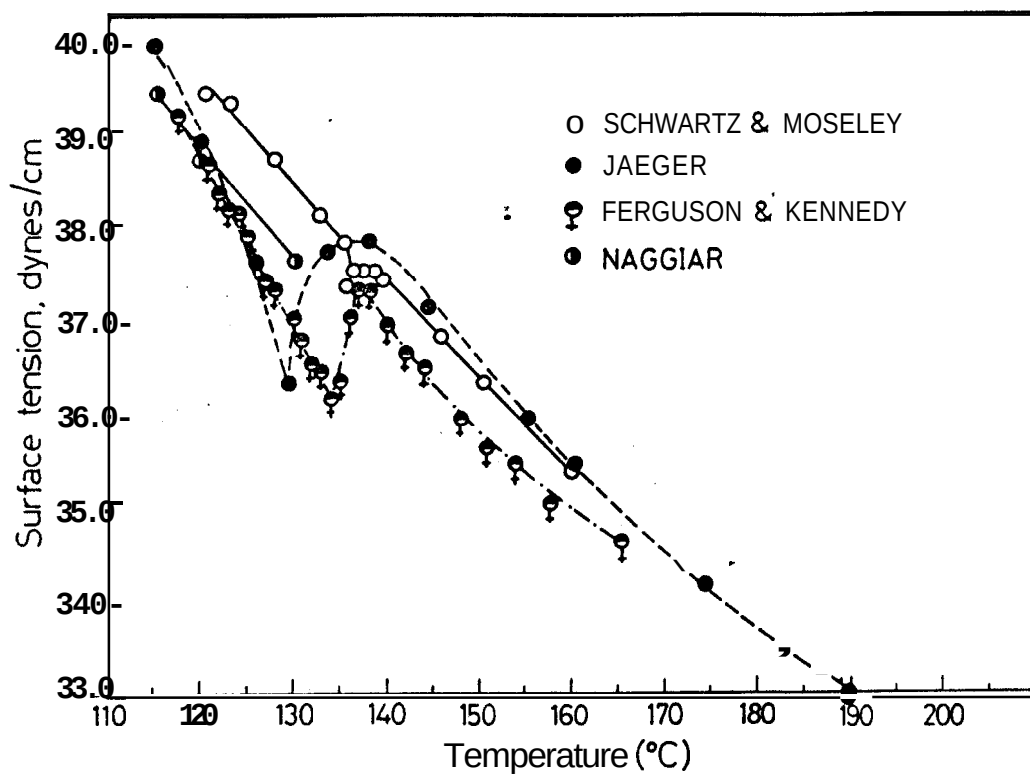


Figure 4.4

Surface tension-temperature characteristic curve for PAA. (After references 2 to 5).

Our curve clearly establishes the idea originally proposed by Croxton and Chandrasekhar⁶ that a pronounced excess order develops at the free surface of a nematic liquid crystal near the **N-I** transition and it continues to exist in the isotropic phase also for a few degrees. In fact we can find a close similarity between our experimental curve and the qualitative form of the γ - T curve (fig. 2.3) proposed by Croxton and Chandrasekhar.

The question arises whether the positive slope in the γ - T curve which develops in the nematic phase, just prior to the **N-I** transition, is due to a reorientation of the molecules at the free surface in the neighbourhood of T_{NI} . The alignment of molecules in the free surface has been studied for PAA using light scattering technique.⁷ It is found that in PAA the molecules lie parallel to the surface and the orientation is independent of temperature. It would appear therefore that the shape of γ - T

curve is not due to **any** molecular reorientation at the surface.

PAP

This is the next higher **homologue** of **PAA** (fig.4.5). The N-I transition temperature of the sample used was **166.6°C**. Tables 4.3 and 4.4 give the values of γ and ρ at different temperatures. The density data are due to Bauer and Bernamont.⁸ The experiments were repeated twice using fresh samples and similar γ -T curves were obtained, the values of γ agreeing to within **1%** in the two cases.

The γ -T curve obtained is given in **fig.4.6**. in this case γ decreases **monotonically** in the nematic phase and there is no **discontinuity** at T_{NI} . The slope of the γ -T curve becomes positive a little later in the isotropic phase. After about **2.5°C** it becomes **negative** again with γ assuming a

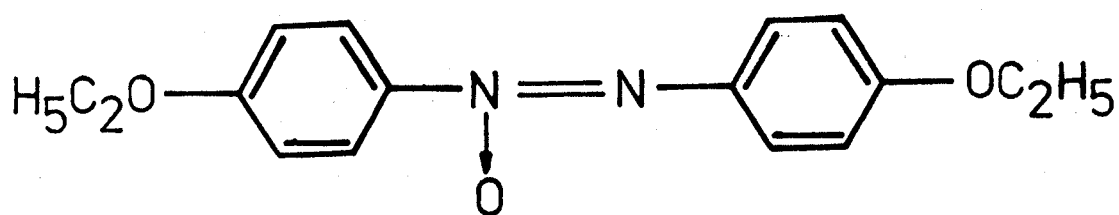


Figure 4.5

Structural formula of p-oxoazobenzene

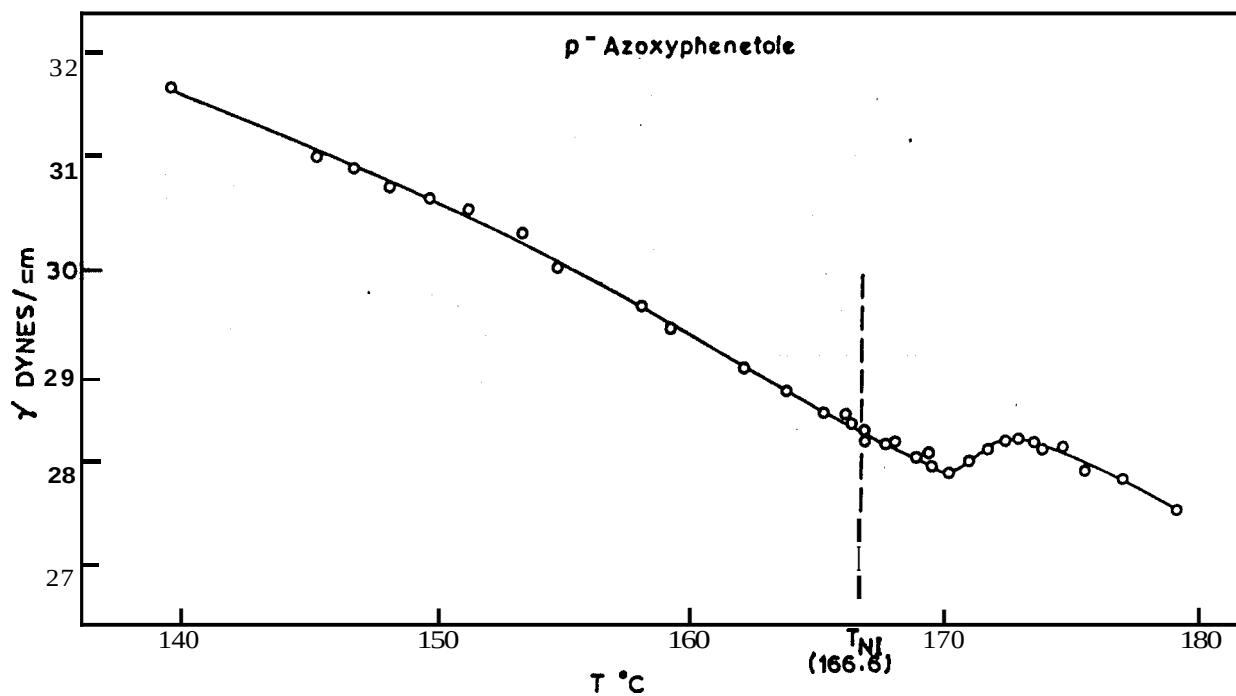


Figure 4.6

Surface tension-temperature characteristic
curve for PAP. (Present investigations).

monotonic decreasing trend.

There have been three earlier measurements^{2,3,5} of γ of this compound as a function of temperature. Again we find a similarity between our curve and the one obtained by Ferguson and Kennedy (see fig. 4.7). There is some similarity with Jaeger's curve also, but it has only one point to indicate the hump (Fig.4.8). The curve obtained by Schwartz and Moseley is completely different as it does not show any hump (Fig.4.8).

In this case we can say that a weak excess order develops in the isotropic phase which manifests in a positive slope for a short range of temperature. The bulk order parameter ' η ' for this compound is found⁹ to be higher than that of PAA. Hence the excess order at the surface may be smaller in this case, when compared to that in PAA, which may be the reason for the smaller hump observed in the γ -I characteristic.

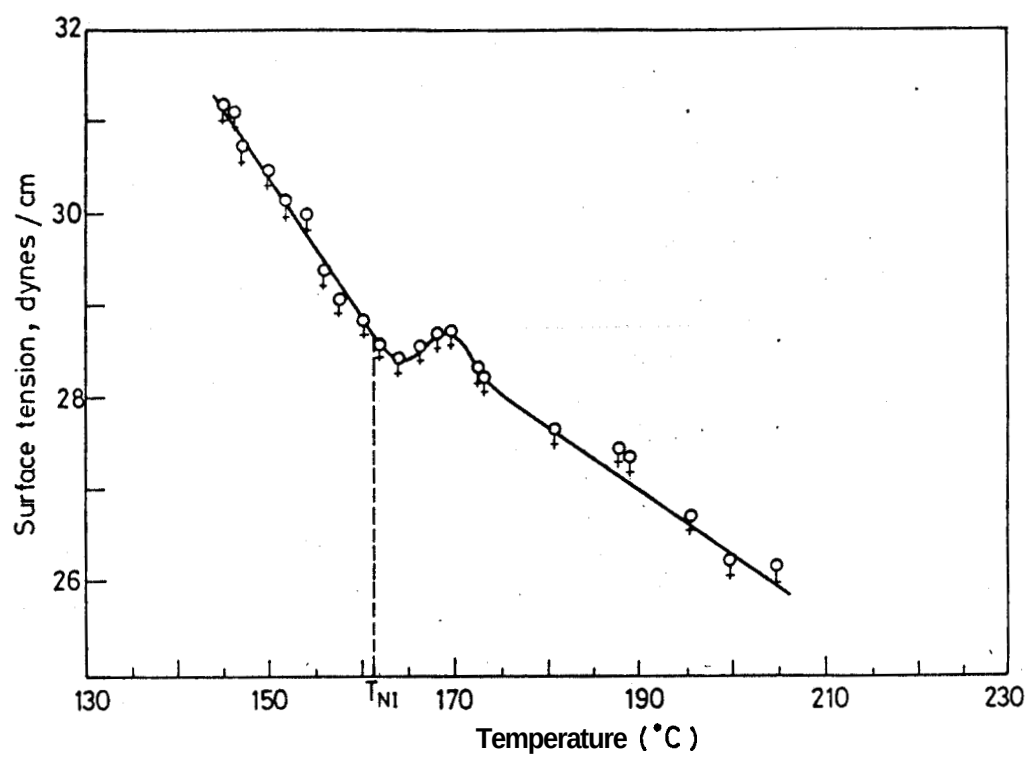


Figure 4.7

Surface tension-temperature characteristic curve **for PAP**. (After **Ferguson** and Kennedy³).

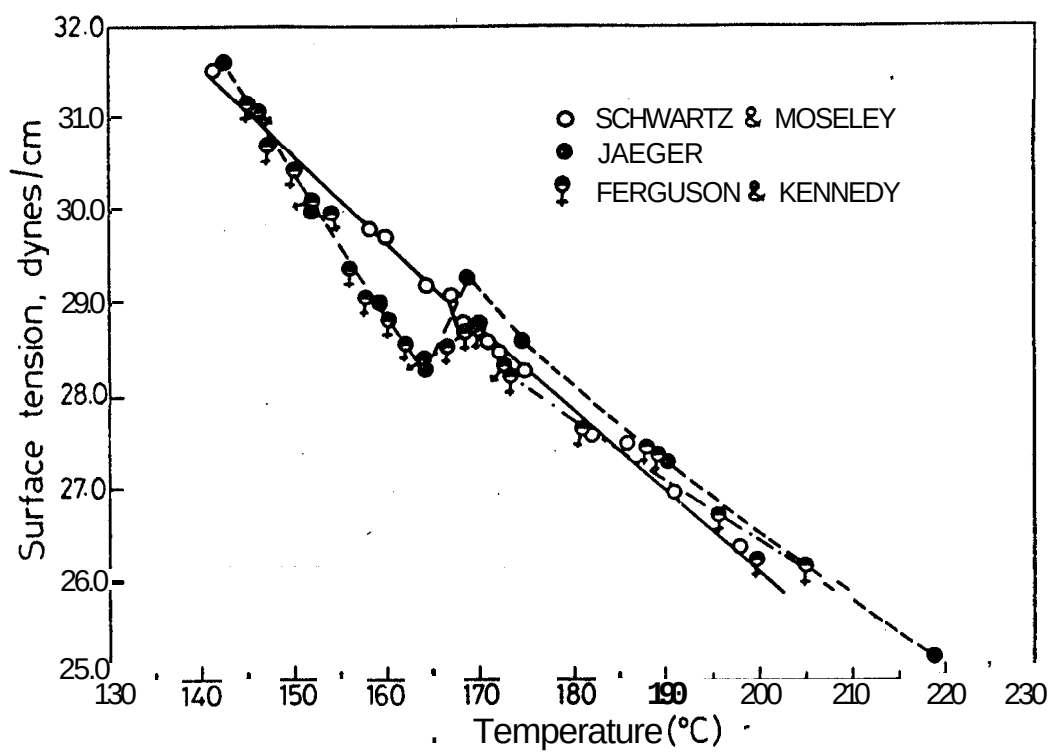


Figure 4.8

Surface tension-temperature characteristic curve for PAP. (After references 2,3,5).

Anisaldazine

This compound has a structure shown in **fig.4.9**. Experiments were done for two samples which had slightly different **M-I** transition temperatures. The transition temperature of the first one was **181.5°C** and that of the second was **182.5°C**. Experiments were repeated twice in each case. However there **was** no difference in the form of the curves obtained when plotted against the relative temperature, $T-T_{NI}$, the agreement between them being within about **1%**. The density data reported by Porter and Johnson¹ (Table 4.6) were used for calculating the values of y (Table 4.5) .

Fig.4.10 gives the γ - T curve obtained in this case. As we can see, the **value** of y decreases initially in the nematic phase. As T_{NI} is approached, the slope becomes positive **with** y increasing **sub-**

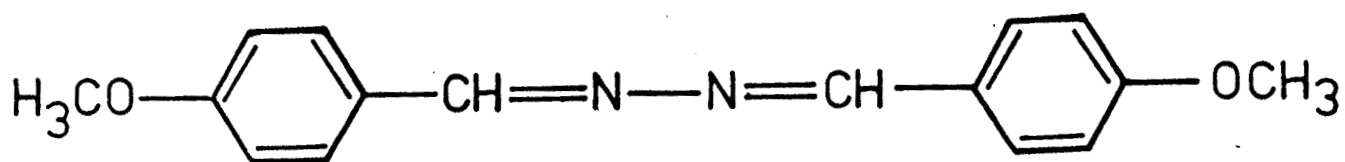


Figure 4.9

Structural formula of **Anisaldazine**

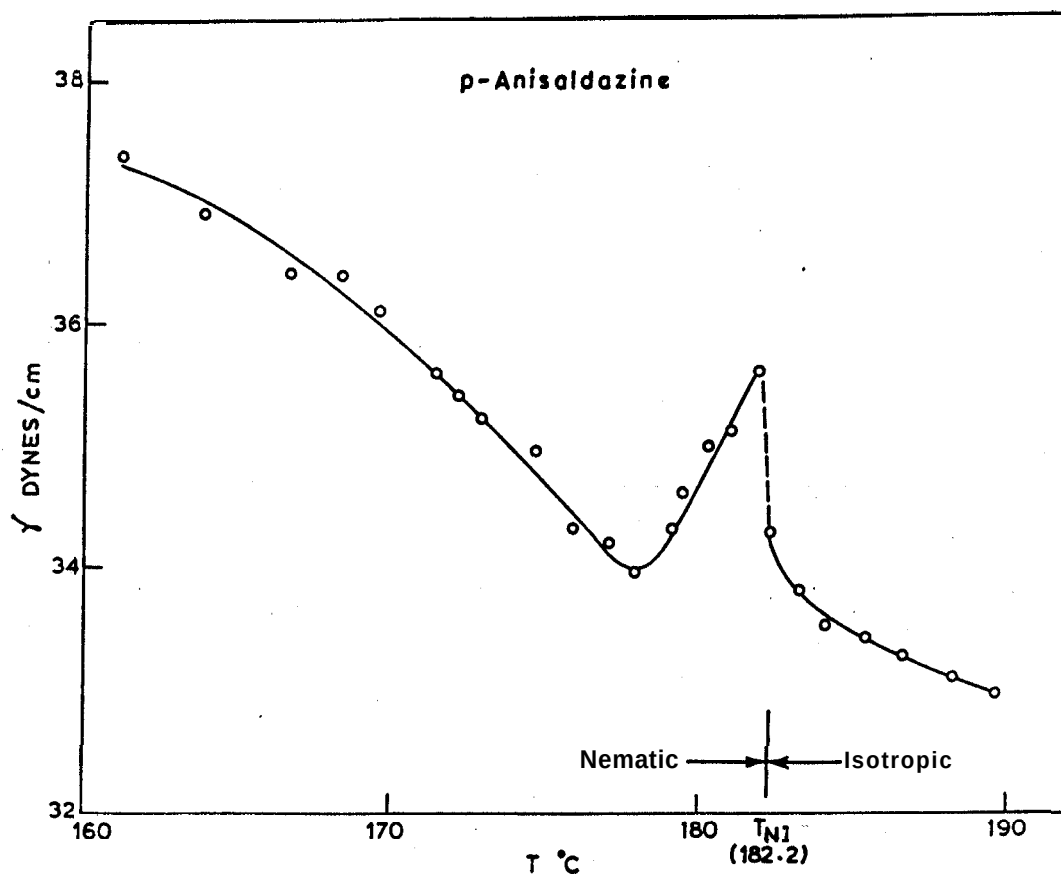


Figure 4.10

Surface tension-temperature characteristic curve for anisaldazine. (Present investigations).

stantially up to the transition point. At the transition there is a discontinuity in the value of γ , with a lower value in the isotropic phase. With further increase of temperature, the monotonic slowly decreasing trend is again exhibited.

The γ - T curve of this compound obtained by Ferguson and Kennedy³ is given in fig. 4.1 1 for comparison. In the nematic phase, the form of the curve obtained by them is almost similar to that of ours. But, at T_{NI} we find a discontinuity in our curve, whereas there is no discontinuity in theirs. In both the cases, the slope is negative in the isotropic phase with a smaller magnitude compared to that in the nematic phase at temperatures much below T_{NI} . The γ - T curve obtained by Jaeger is given in fig. 4.1 2. Though this curve does not have points along the increasing branch, it does indicate a positive slope in the vicinity of T_{NI} .

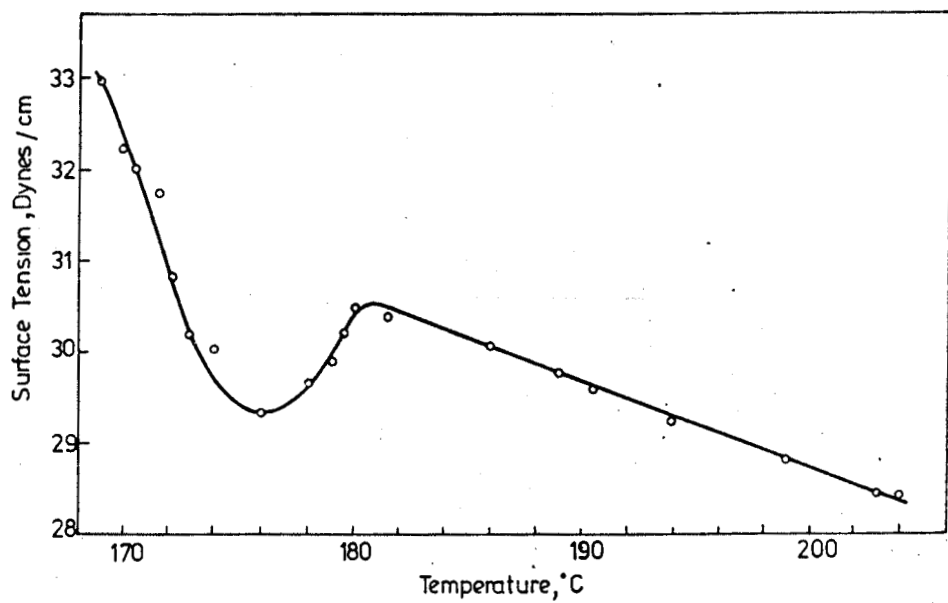


Figure 4.11

Surface tension-temperature characteristic
for anisaldazine. (After Ferguson & Kennedy.³)

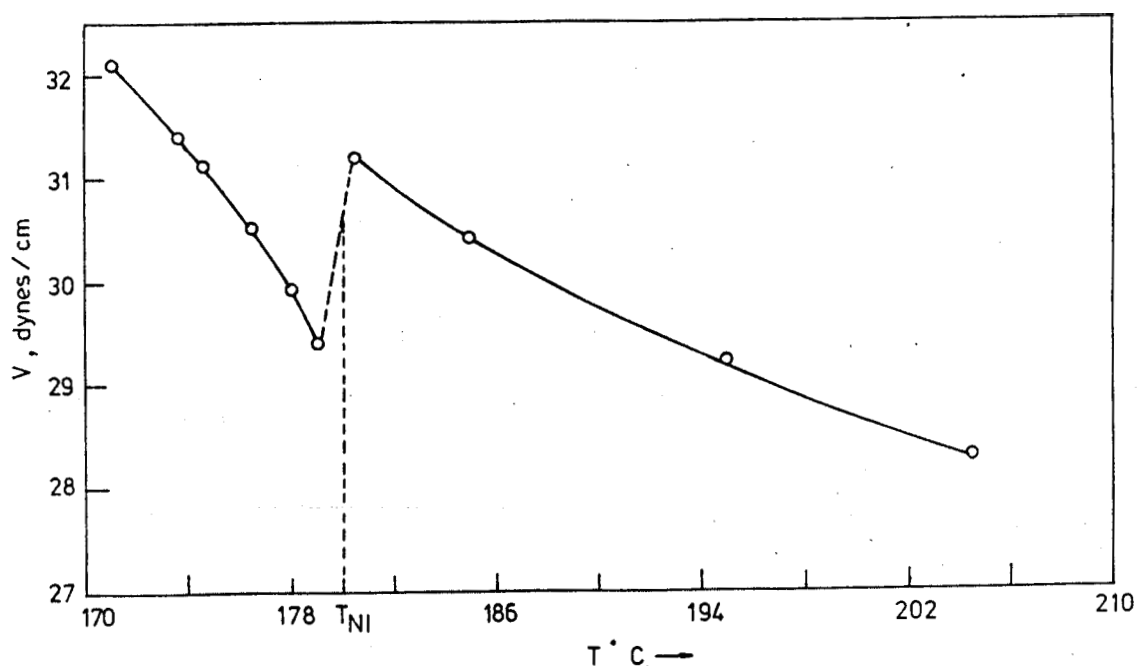


Figure 4.12

Surface tension-temperature characteristic curve for anisaldazine. (After Jaeger²).

The behaviour of the γ -T characteristic suggests that a pronounced enhancement in the surface excess order develops in the nematic phase as the N-I transition temperature is approached. In the isotropic phase a **weak** surface order remains which may be responsible for the decrease in the magnitude of the negative slope as compared with that in the nematic phase much below T_{NI} . We find a similarity between our curve and the qualitative form of the curve proposed by Croxton and Chandrasekhar (Fig. 2.2).

MBBA

This is a room temperature nematic liquid crystal with the **structural** formula given in fig. 4.13. The N-I transition temperature of the sample used was 43.2°C . For calculating γ , the density values were taken from the data reported by Gulari and Chu.¹⁰ Tables 4.7 and 4.8 give the values of γ and ρ .

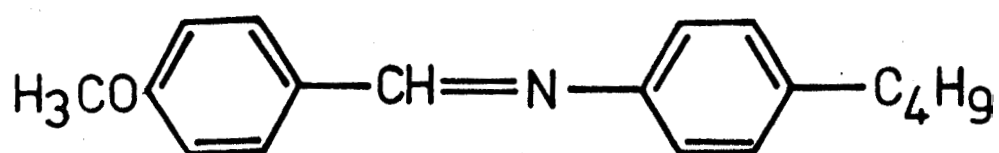


Figure 4.13

Structural formula of 4-methoxybenzylidene-
4'-butylaniline

A problem that was encountered during the experiments using this compound was that the transition temperature was highly dependent on factors like humidity, shelf life, etc. It was necessary to carry out a **vacuum** sublimation of the sample and experiment was conducted immediately thereafter, before there was any chemical degradation,

In this case measurements were repeated twice with **fresh** samples. The two experiments gave values which agreed within about 1%. The γ -T curve is shown in **fig.4.14**. This curve is somewhat similar to that of **anisaldazine**, but for some differences: firstly in this case there is no marked discontinuity in the value of γ at T_{NI} ; secondly the rise in the value of γ before T_{NI} is less.

There has been another experimental study of the γ -T characteristic of this compound by Langevin,¹¹

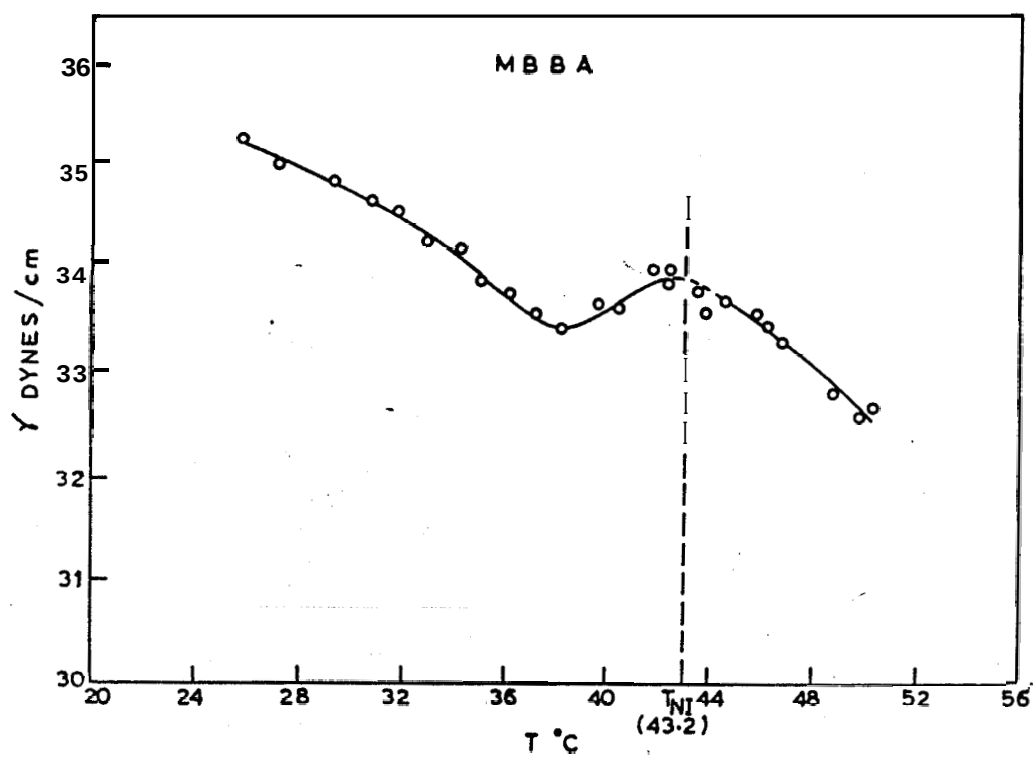


Figure 4.14

Surface tension–temperature characteristic
curve for MBBA. (Present investigations).

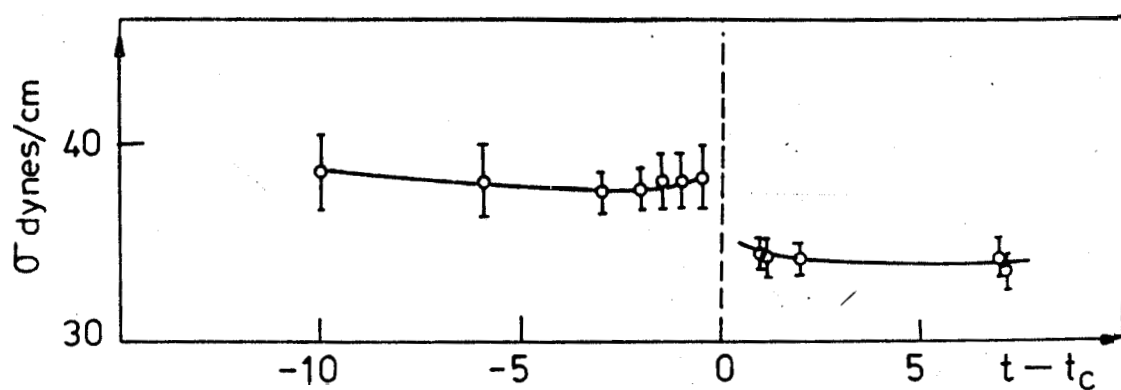


Figure 4.15

Surface tension-temperature characteristic curve for MBBA. (After Langevin¹¹).

who used the light scattering technique. The γ -T curve is shown in fig. 4.15. This curve shows a discontinuity in the value of γ at T_{NI} with a lower value in the isotropic phase. But it should be noted that the error bar is very large in this case and there are no points close to T_{NI} in the curve. Anyhow both the curves agree as far as the positive slope occurring before T_{NI} is considered. The positive slope indicates the development of excess surface order prior to the transition.

5CB

This is also a room temperature liquid crystal, which has a structure shown in fig. 4.16. The N-I transition temperature of the sample used was 35.0°C. The density value for calculating γ were taken from the data of Gannon and Faber.¹² Experiments were repeated three times using fresh samples and the values agreed to within 1%.

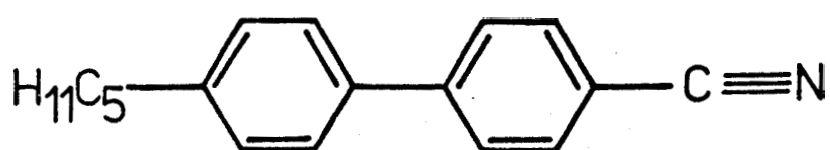


Figure 4.16

Structural formula of 4'-n-pentyl-
4-cyanobiphenyl

As we can see in **fig.4.17**, the γ -T curve is different from those of the other compounds presented in this chapter. In this case we find that the slope is positive throughout the range of measurements in the nematic phase. At T_{NI} there is a jump in the value of γ with a higher value in the isotropic phase, as in the case of PAA. In the isotropic phase, initially the slope of the curve tends to be positive but soon it becomes negative with γ assuming a monotonic decreasing trend.

When the measurements on **this** compound were in progress, the γ -T curve of the same compound was reported by Gannon and Faber,¹² who used the Wilhelmy plate method. The γ -T curve obtained by them is given in **fig.4.18** for comparison. We can see that the two curves are in excellent agreement with each other.

Because of the strong polar group at **one** end, the molecules of this compound may be expected to

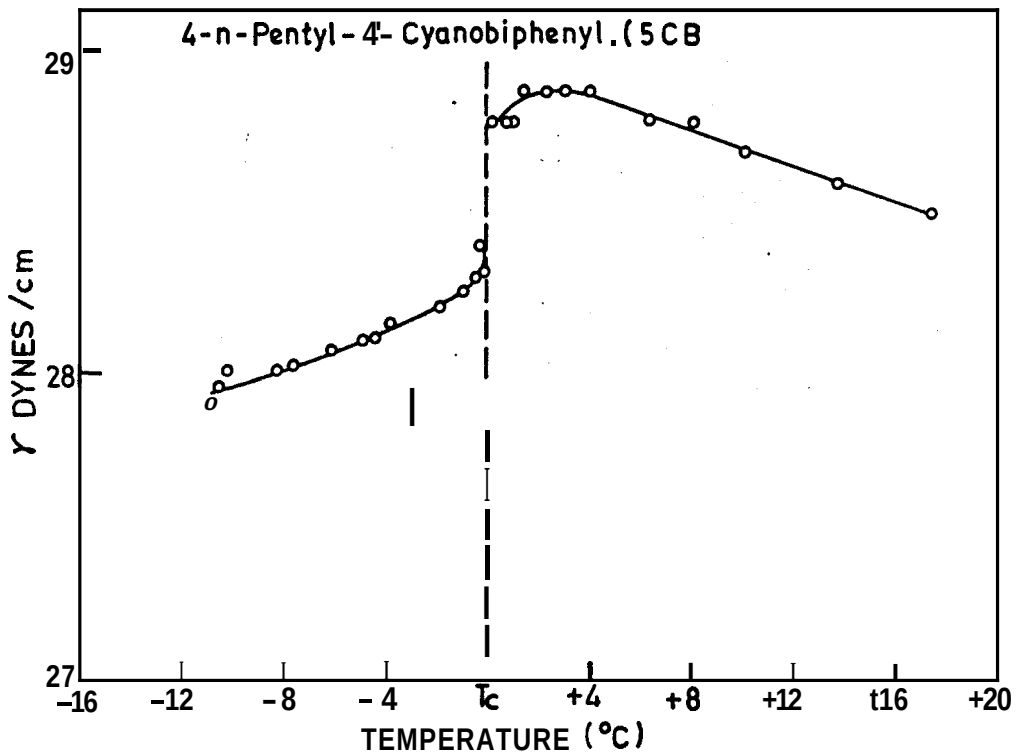


Figure 4.17: Surface tension-temperature characteristic curve for 5CB (Present investigations).

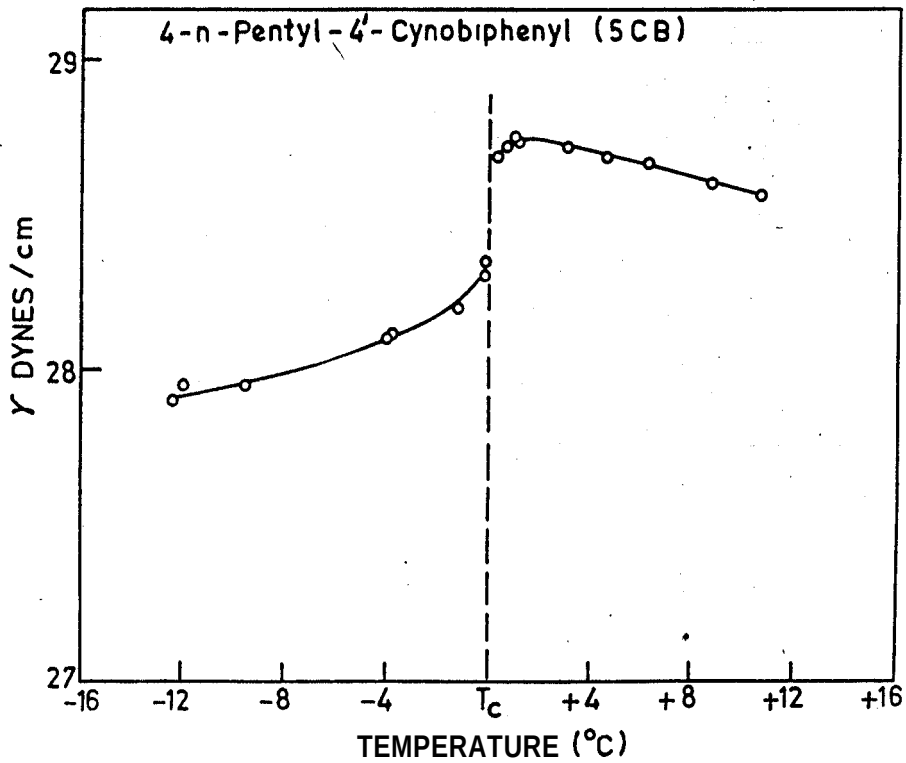


Figure 4.18: Surface tension-temperature characteristic curve for 5CB (After Gannon and Faber¹²).

align perpendicular to the free surface, as predicted by Parsons,¹³ Moreover, **this** compound is known to have cybotactic **groups**.¹⁴ Hence, though it is a nematic, smectic A like **behaviour** may be expected **near** the surface, **as** we shall see in the next chapter. The slope of the $y-l$ curve is found to be positive for a large temperature range in the smectic phase, Hence we **may conclude** that the **nematic** phase of **5CB** exhibits a smectic A like behaviour **as far as** the surface tension is concerned.

In conclusion it can be said that our results on these **compounds are** in qualitative agreement with the theoretical predictions of Croxton **and** **Chandrasekhar**, ^{also of} **and** Parsons. **As** the experiments were conducted under thermodynamic **equilibrium conditions** and as there was no influence of the solid surface on the molecular **alignment** at the free surface, the results suggest **unambiguously** that

an excess order develops at the free surface of nematic liquid crystals, In some systems it develops in the vicinity of N-I transition and in some other systems like 5CB it develops much earlier in the nematic phase. The excess order persists in the isotropic phase also for a certain range of temperature.

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Table 4.1

Surface tension of p-azoxyanisole

Temperature °C	γ dyne cm ⁻¹	Temperature °C	γ dyne cm ⁻¹
119.7	37.1	134.0	34.5
120.5	37.2	134.6	34.6
121.8	36.9	135.3	35.2
122.8	26.6	136.2	35.4
125.2	36.2	137.2	35.9
127.0	35.7	138.4	35.9
128.0	35.5	139.3	36.0
128.4	35.3	139.9	35.7
130.1	35.0	140.5	35.6
131.4	34.7	141.4	35.5
132.9	34.6	142.1	35.0
133.5	34.6		

Table 4.2

Density of p-azoxyanisole

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
119.7	1.1652	134.0	1.1504
120.5	1.1645	134.6	1.1495
121.8	1.1632	135.3	1.1439
122.8	1.1622	136.2	1.1436
125.2	1.1598	137.2	1.1427
127.0	1.1580	138.4	1.1416
128.0	1.1572	139.3	1.1408
128.4	1.1568	139.9	1.1403
130.1	1.1549	140.5	1.1397
131.4	1.1536	141.4	1.1389
132.9	1.1518	142.1	1.1383
133.5	1.1510		

Table 4.3

Surface tension of para-azoxyphenetole

Temperature °C	γ dyne cm ⁻¹	Temperature °C	γ dyne cm ⁻¹
139.4	31.8	167.5	28.3
145.2	31.2	168.0	28.3
146.6	31.0	168.8	28.1
147.9	30.8	169.1	28.3
149.6	30.7	169.3	28.0
151.1	30.6	170.0	28.0
153.2	30.3	170.8	28.1
154.6	30.0	171.5	28.2
158.0	29.6	172.3	28.3
159.1	29.4	172.6	28.3
162.0	29.0	173.4	28.3
163.7	28.8	173.7	28.2
165.2	28.6	174.4	28.2
165.9	28.6	175.4	28.0
166.3	28.5	176.8	27.9
166.8	28.4	179.2	27.6
166.7	28.3		

Table 4.4**Density of para-asoxyphenetole**

Temperature °C	density gm/cc	Temperature °C	density gm/cc
139.4	1.0955	167.5	1.0595
145.2	1.0900	168.0	1.0590
146.6	1.0890	168.8	1.0585
147.9	1.0875	169.1	1.0580
149.6	1.0860	169.3	1.0580
151.1	1.0845	170.0	1.0575
153.2	1.0825	170.8	1.0565
154.6	1.0810	171.5	1.0560
158.0	1.0770	172.3	1.0555
159.1	1.0760	172.6	1.0550
162.0	1.0730	173.4	1.0545
163.7	1.0710	173.7	1.0540
165.2	1.0695	174.4	1.0535
165.9	1.0685	175.4	1.0525
166.3	1.0680	176.8	1.0515
166.8	1.0600	179.2	1.0490
166.7	1.0605		

Table 4.5

Surface tension of anisaldazine

Temperature °C	γ dyne cm ⁻¹	Temperature °C	γ dyne cm ⁻¹
161.2	37.4	179.2	34.3
163.9	36.9	179.5	34.6
166.8	36.4	180.4	35.0
168.4	36.4	181.3	35.1
169.7	36.1	182.1	35.6
171.5	35.6	182.4	34.3
172.2	35.4	183.4	33.8
172.9	35.2	184.1	33.5
174.8	34.9	185.5	33.5
176.0	34.3	186.7	33.3
177.1	34.2	188.2	33.2
178.1	34.0	189.7	33.0

Table 4.6

Density of Anisaldazine

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
161.2		179.2	1.0448
163.9	1.0621	179.5	1.0444
166.8	1.0588	180.4	1.0433
168.4	1.0571	181.3	1.0420
169.7	1.0556	182.1	1.0343
171.5	1.0536	182.4	1.0341
172.2	1.0527	183.4	1.0332
172.9	1.0519	184.1	1.0326
174.8	1.0498	185.5	1.0314
176.0	1.0484	186.7	1.0304
177.1	1.0471	188.2	1.0291
178.1	1.0460	189.7	1.0278

Table 4.7

Surface Tension of MBBA

Temperature °C	γ dyne cm ⁻¹	Temperature °C	γ dyne cm ⁻¹
25.8	35.3	41.9	34.0
27.2	35.1	42.4	33.9
29.3	34.9	42.8	34.0
30.8	34.7	43.5	33.8
31.9	34.6	43.9	33.7
33.0	34.3	44.6	33.7
34.3	34.3	45.6	33.6
35.0	33.9	46.1	33.5
36.2	33.8	46.8	33.3
37.3	33.6	48.8	32.8
38.3	33.5	49.9	32.5
39.6	33.7	50.4	32.6
40.6	33.7		

Table 4.8

Density of MBBA

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
25.8	1.0471	41.9	1.0307
27.2	1.0457	42.4	1.0303
29.3	1.0435	42.8	1.0299
30.8	1.0420	43.5	1.0273
31.9	1.0409	43.9	1.0269
33.0	1.0398	44.6	1.0263
34.3	1.0385	45.6	1.0254
35.0	1.0378	46.1	1.0250
36.2	1.0366	46.8	1.0244
37.3	1.0355	48.8	1.0227
38.3	1.0345	49.9	1.0217
39.6	1.0332	50.4	1.0213
40.6	1.0322		

Table 4.9

Surface Tension of 5CB

Temperature °C	γ dyne/cm	Temperature °C	γ dyne/cm
24.2	27.9	34.8	28.3
24.5	27.9	35.2	28.8
24.9	28.0	35.8	28.8
26.8	28.0	36.2	28.8
27.4	28.0	36.5	28.9
28.8	28.1	37.2	28.9
30.0	28.1	37.5	28.9
30.5	28.1	38.2	28.9
31.1	28.2	41.4	28.8
33.0	28.2	43.2	28.8
33.9	28.3	45.1	28.7
34.4	28.3	48.8	28.6
34.6	28.4	52.2	28.5

Table 4.10

Density of 5CB

Temperature °C	Density gm/cc	Temperature °C	Density gm/cc
24.2	1.0088	34.8	0.9989
24.5	1.0086	35.2	0.9956
24.9	1.0082	35.8	0.9941
26.8	1.0064	36.2	0.9937
27.4	1.0059	36.5	0.9934
28.8	1.0045	37.2	0.9930
30.0	1.0035	37.5	0.9928
30.5	1.003	38.2	0.9923
31.1	1.0024	41.4	0.9903
33.0	1.0006	43.2	0.9892
33.9	0.9998	45.1	0.9880
34.4	0.9993	48.8	0.9857
34.6	0.9991	52.2	0.9836