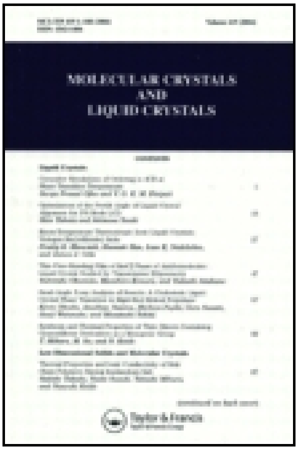
This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 19 February 2013, At: 14:24
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Viscosity Coefficients of Some Nematic Liquid Crystals

A. G. Chmielewski [a]

[a] Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Version of record first published: 20 Apr 2011.

To cite this article: A. G. Chmielewski (1986): Viscosity Coefficients of Some Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 132:3-4, 339-352

To link to this article: http://dx.doi.org/10.1080/00268948608079552

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1986, Vol. 132, pp. 339–352
0026-8941/86/1324-0339/$20.00/0
© 1986 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Viscosity Coefficients of Some Nematic Liquid Crystals†

A. G. CHMIELEWSKI
Institute of Nuclear Chemistry and Technology, Warsaw, Poland

(*Received July 3, 1984*)

The viscosity coefficients η_1, η_2 and η_3 of 4-n-pentyl-4'-cyanobiphenyl (5CB), 4-n-octyl-4'-cyanobiphenyl (8CB), 4-n-pentyloxy-4'-cyanobiphenyl (5OCB), and 4-n-octyloxy-4'-cyanobiphenyl (8OCB) have been determined over their nematic phases. Using literature data for the temperature dependence of the order parameter S, given for 5CB and 8CB, a relation between the anisotropy of viscosity coefficients and parameter S is discussed. Two models; first the Imura-Okano model, and the second, assuming a dependence between the term $(\eta_i/\eta_{iso} - 1)$ and the order parameter, are analysed. For the second assumption much higher values of the correlation coefficients have been obtained. On the base of our own and Skarp's data for 5CB, it has been proved that the assumption of $\alpha_3 \cong 0$ made for the elongated molecules is correct. Following this some anomalies observed for 8CB are discussed. The linear dependence obtained between the viscosity coefficients and the order parameter is analogous to the equations obtained by the author for the anisotropy of other transport properties, i.e. diffusivity of impurities and heat conduction, for the same liquid crystals.

INTRODUCTION

Despite the fact that the anisotropy of viscosity for nematic liquid crystals was stated by Mięsowicz[1] over forty years ago the experimental data that would allow the problem to be solved completely are still insufficient. Relatively complete studies have been carried out for the compound 4-methoxybenzylidene-4'-n-butylaniline (MBBA). The earliest results of investigations obtained for this compound were published by Gähwiller[2] but later they were questioned by Summerford et al.,[3] de Jeu[4] and Kneppe and Schneider.[5] However, the results published by these latter authors are not in full accordance

†Presented at the Tenth International Liquid Crystal Conference, York, July 15-21, 1984.

with each other. Also different results have been obtained by Kashkin and Cumakova.[6]

Only two of the mentioned papers give the temperature dependence of three viscosity coefficients. The other studies do not go beyond measuring the coefficients at one temperature only. Investigations of the cyanobiphenyl group of compounds have been carried out by Sharp,[7] Leger[8] and Kneppe et al.[9] The hydrodynamic description of liquid crystals has been developed by Ericsen[10,11] and Leslie.[12,13,14] The general approach in this case is similar to that adopted for deriving the constitutive equations for isotropic liquid. It consists of formulating and developing the balance equations of nematic liquid crystals.

EXPERIMENTAL

The investigations have been carried out for four substances of the cyanobiphenyl homologues. The temperature range examined corresponds to the nematic phase temperatures. The following compounds and temperatures have been examined:

4-n-pentyl-4'-cyanobiphenyl (5CB)

$$S \xrightarrow{22°C} N \xrightarrow{34°C} IL$$

4-n-octyl-4'-cyanobiphenyl (8CB)

$$S \xrightarrow{21°C} SM \xrightarrow{32,5°C} N \xrightarrow{40°C} IL$$

4-n-pentyloxy-4'-cyanobiphenyl (5OCB)

$$S \xrightarrow{47°C} N \xrightarrow{66,3°C} IL$$

4-n-octyloxy-4'-cyanobiphenyl (8OCB)

$$S \xrightarrow{54°C} SM \xrightarrow{66,5°C} N \xrightarrow{79,8°C} IL$$

The compounds used were synthesized in the Institute of Organic Chemistry and Technology, Warsaw Technical University.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

For determining the three viscosity coefficients proposed by Mięsowicz, a slot viscosimeter was used. The complete device is shown in Figure 1. The measuring slot has a rectangular cross-section 7 × 0.3 mm and a length of 60 mm. The whole apparatus is shown in Figure 2.

The viscosimeter was calibrated using different standard liquids. The measurements of the viscosity coefficients were carried out for different positions of the electromagnet with respect to the measuring slot. The magnetic field intensity was 0.4T.

In case of molecules aligned perpendicular to the flow vector (η_1, η_3) the flow-forcing overpressure was around 10 Pa while in case of parallel orientation (η_2) the corresponding overpressure values were of the order of 0.7 kPa. The accuracy of the pressure measurements was ±0.05 Pa and the thermostatic temperature control gave a 0.1°C stability.

RESULTS

The results of measurements are shown in Figures 3, 4, 5 and 6. They are also presented in the diagram on a semilog scale. The diagram

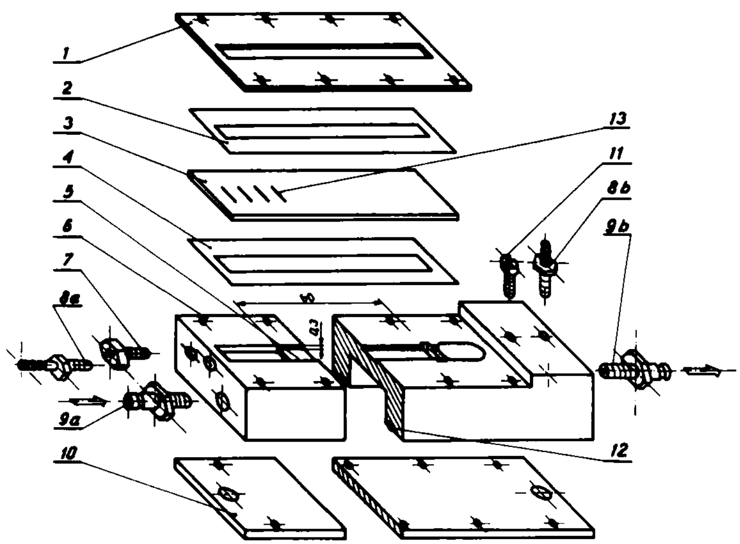


FIGURE 1. The slot viscosimeter where: 1-brass plate; 2-teflon washer; 3-glass plate; 4-teflon washer; 5-measuring slot; 7-thermocouple packing; 8a,8b-the overpressure system joint; 9a,9b-thermostatic liquid inlet and outlet; 10-cover of the thermostatic liquid tank; 11-hole screw plug of the examined liquid inlet; 12-seal; 13-measuring scale marks. (Dimensions in mm).

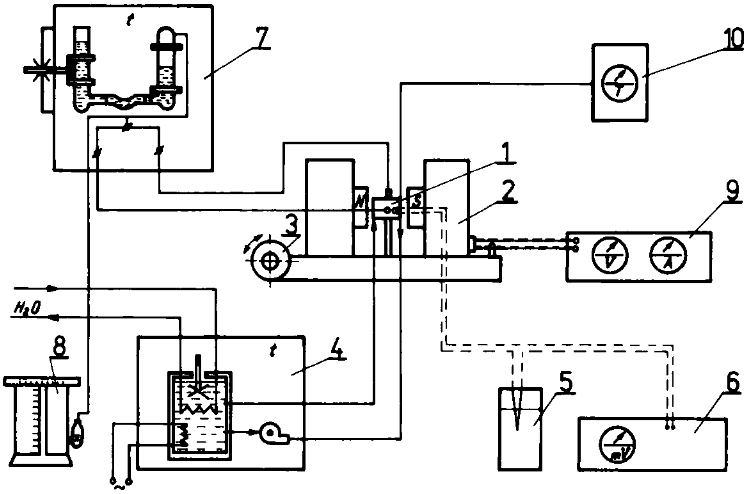


FIGURE 2. Test stand for measuring the viscosity coefficients η_1, η_2 and η_3. 1-slot viscosimeter; 2-electromagnet; 3-electromagnet rotation device; 4-thermostat; 5-Dewar flask; 6-milivoltmeter connected with a thermocouple; 7-manostat; 8-manometer; 9-power supply for the electromagnet; 10-teslometer.

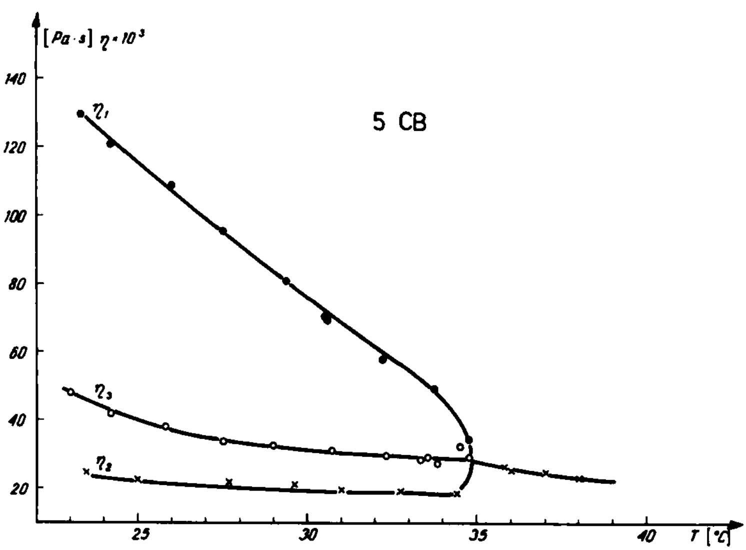


FIGURE 3. Temperature dependence of the viscosity coefficients for 5 CB.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

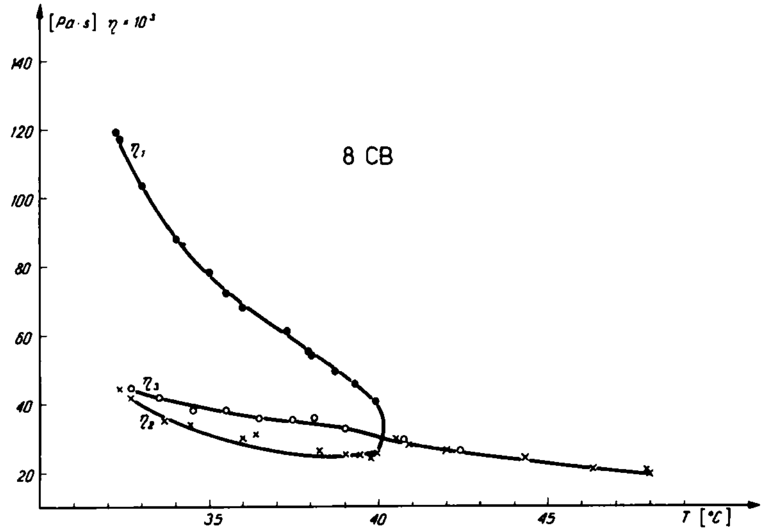


FIGURE 4. Temperature dependence of the viscosity coefficients for 8 CB.

shows the dependence of viscosity plotted against the dimensionless temperature parameter, Figure 7.

Certain anomalies have been observed for the curve $\eta_2 = f(T)$ of 8 CB. Some authors[9] have even reported an intersection of this curve with that for η_3. Such a phenomenon has not been observed in the

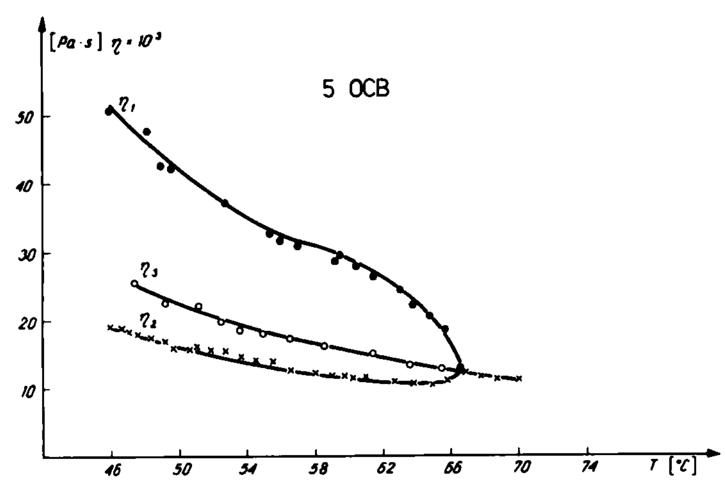


FIGURE 5. Temperature dependence of the viscosity coefficients for 5OCB.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

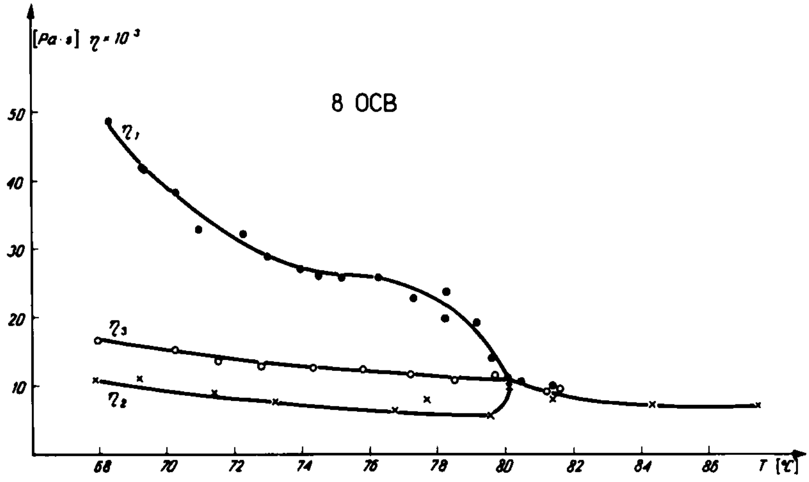


FIGURE 6. Temperature dependence of the viscosity coefficients for 8OCB.

present work. The anomaly may be connected with the possibility of the existence of smectic structures above the temperature of the smectic-nematic phase transition.

From the analysis of the viscosity curves we can state that the oxygen-free compounds 5 and 8CB are characterized by considerably higher values of the viscosity coefficients in comparison with the two alkyloxy compounds 5 and 8OCB.

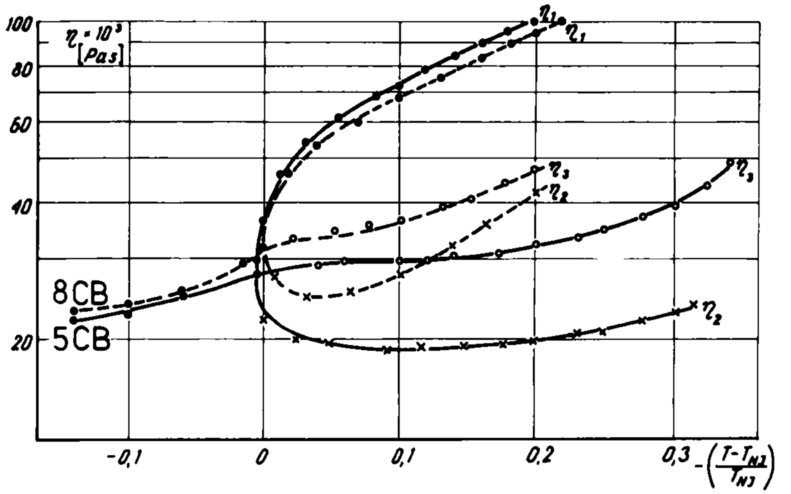
COEFFICIENTS OF THE TANGENTIAL STRESS-TENSOR

The equations relating the measured viscosity coefficients with the coefficients of the tangential stress-tensor (Leslie's coefficients) have the following form:

$$\eta_1 = \frac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2) \qquad (1)$$

$$\eta_2 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6) \qquad (2)$$

$$\eta_3 = \frac{1}{2}\alpha_4 \qquad (3)$$



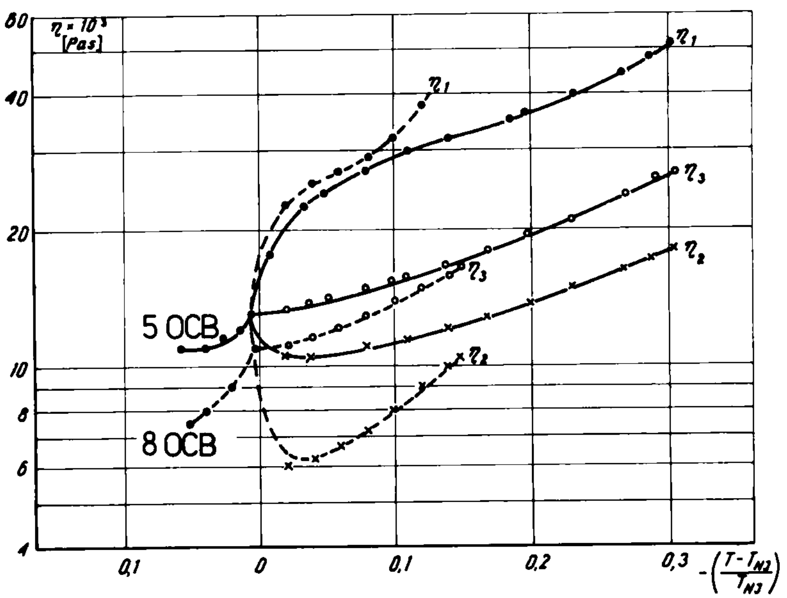


FIGURE 7. Viscosity coefficients for the nematic phase of the liquid crystal substances studied.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

and also according to the Parodi[15] relationship:

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \tag{4}$$

Further, solution of the equation system is feasible if, in the case of the oblong molecules of mesogen being considered, one assumes

$$\alpha_3 \cong 0 \tag{5}$$

The assumption adopted can be verified on the grounds of the results obtained by Skarp,[9] who has determined the values of α_2 and α_3 for 5CB. These data are listed in the Table I.

The values of α_3, according to Skarp, vary within the range of -4.0 to -2.2×10^{-3} Pa·s, thus being lower than the differences between the α_2 coefficients obtained by Skarp and author of the present paper. Considering this, they can be regarded as very close to the measurement error. Certain precaution should, however, be maintained in case of 8CB. The anomalies occurring in the η_2 values are clearly visible in the curve α_6 as a $f(T)$. The temperature dependence of the α coefficients are shown in Figure 8.

VERIFICATION OF THE IMURA-OKANO MODEL

Imura and Okano[16] have worked out a model correlating the coefficients of the stress-tensor and also viscosity coefficients η_i with the order parameter S. The authors have assumed that the widely applied exponential Eyring's function for the viscosity of a liquid also applies to a certain limited temperature range (of the order ≤30°C) below the point of the nematic-isotropic phase transition:

$$\eta_{iso} = \frac{1}{2}\alpha_4 = \eta_o \exp(E/kT) \tag{6}$$

then:

$$\eta_1 = \eta_{iso} + \left(\frac{1}{4}\alpha + \frac{3}{2}B_1 S\right) \tag{7}$$

$$\eta_2 = \eta_{iso} + \left(\frac{1}{4}\alpha - \frac{1}{2}B_1 S\right) \tag{8}$$

TABLE I

Values of the coefficients α_3 and α_2 for 5 CB.

T[°C]	23.5	25	26	27	28.5	29.5	30	31.5	32.5	33	34	34.4	
$-\alpha_3$ [Pa.s.10^3]	-	-	4.0	-	-	3.4	-	-	2.8	-	2.2	-	Skarp[7]
$-\alpha_2$ [Pa.s.10^3]	-	-	75.6	-	-	55.4	-	-	38	-	26		
$-\alpha_2$ [Pa.s.10^3]	104	93	87.5	79	68	-	57	46	-	36	27.5	21.5	this work

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

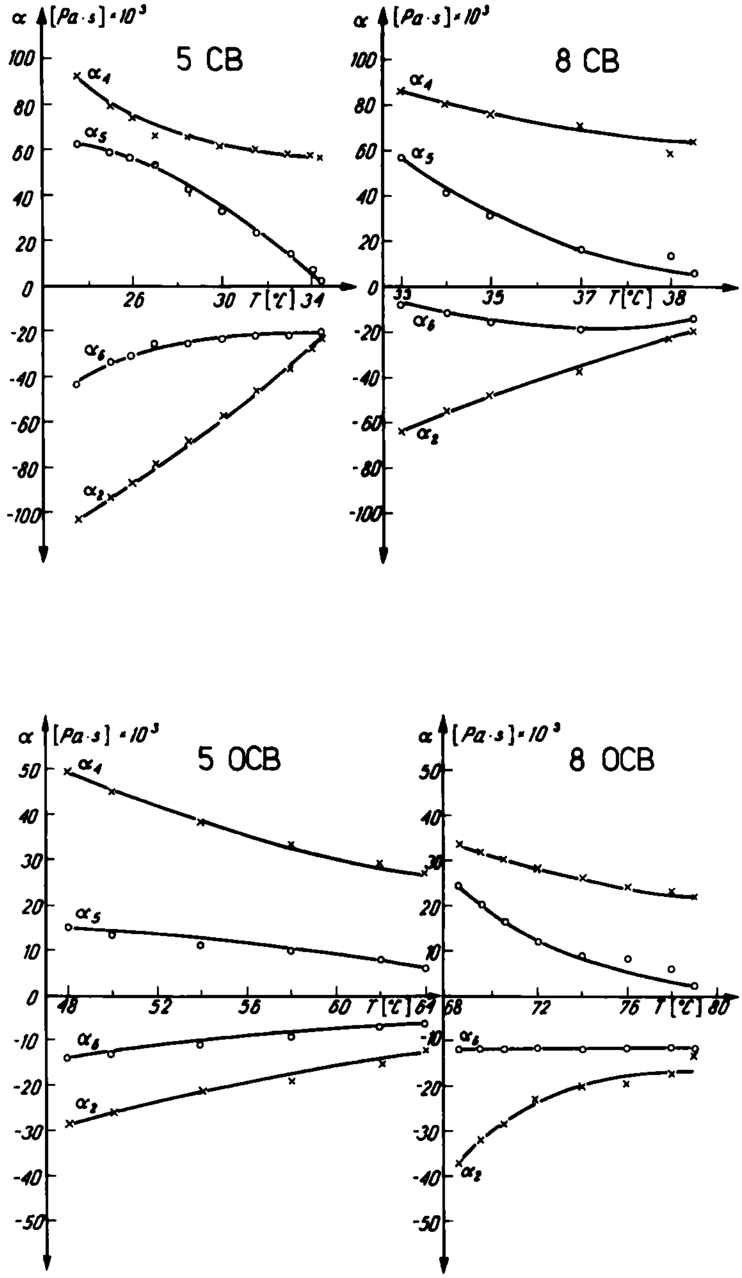


FIGURE 8. The temperature dependence of the α coefficients of the Leslie's tangential stress-tensor.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

$$\eta_3 = \eta_{iso} - \frac{1}{2}\alpha S \tag{9}$$

where α and B_1 are constants little depending on temperature. According to the relationships (7) and (8) the following equation occurs:

$$\eta_1 - \eta_2 = 2B_1S \tag{10}$$

Thus the temperature dependence of the difference $\eta_1 - \eta_2$ on the S-parameter should form a straight line, since, as the authors suggest, B_1 is practically independent of temperature.

The temperature dependence of the order parameter S has been given in literature for 5CB[17,18,19,20,21,22] and for 8CB.[17,22] It should be emphasized, however, that there are remarkable differences between the published data. In the current calculations the results published by Horn[17] have been adopted. The results are collected in the Table II.

According to Eq. 10 the straight line should pass through the zero point of coordinates. On the account of the measurement errors inherent in the determination of $\Delta\eta$ and S values, certain shift can be observed i.e. column 2 in Table II. The correlation coefficents are, however, satisfactorily high, which permits us to conclude that the Imura-Okano model is totally applicable for relating the viscosity coefficients with the order parameter S.

APPLICATION OF THE PHENOMENOLOGICAL ANALOGIES FOR CORRELATING THE η_i AND S COEFFICIENTS

The order parameter S is normally determined from measurements of either the diamagnetic constant or the electric polarisation anisotropy in the sample examined. The measurements are carried out first in the solid phase and then in the liquid crystal phase.[23] The following general relationship is then applied:

TABLE II

Straight-line coefficients for the function $\Delta\eta = f(S)$

Compound	(1) Straiqht-line [Pa.s × 10³]	(2) Intersection point $\Delta\eta(S = 0)$	(3) Correlation coeff.
5CB	$\Delta\eta$ = 80.07 S	− 2.8	0.902
8CB	$\Delta\eta$ = 156.06 S	− 8.1	0.903

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

$$S = \frac{a_{\parallel} - a_{\perp}}{a^s_{\parallel} - a^s_{\perp}} \tag{11}$$

where $a^s_{\parallel} - a^s_{\perp}$ represents anisotropy of a solid ($S = 1$) and $a_{\parallel} - a_{\perp}$ is the anisotropy of a liquid crystal (O<S<1).

Viscosity of a solid is, however, a term rather difficult to imagine but relationships of this kind describing a correlation between η_i and S in a formal way are presented in literature.[9] Usually they have the following form:

$$S = \frac{\eta_i - \eta_{iso}}{\eta^s_i - \eta_{iso}} \tag{12}$$

where η_{iso} is defined by the Eq. 6 whereas η^s_i is the viscosity of aligned sample for $S = 1$.

The notion of η_{iso} is a formal extrapolation of the function describing the temperature dependence of viscosity for an isotropic phase into the temperature region in which a nematic phase occurs. A similar exponential temperature dependence in the region of the nematic phase can be formally adopted for η^s_i. Thus the term η^s_i/η_{iso} practically will not depend on temperature. Having transformed Eq. 12 we obtain the following expression:

$$\frac{\eta_i}{\eta_{iso}} - 1 = AS \tag{13}$$

Analytical forms of the straight lines representing the relationships for 5CB and 8CB, i.e. the compounds for which the S coefficient values have been found in literature are given in Table III. High values of the correlation coefficients show a good agreement between the relationship proposed and the experimental data. A slight deviation, which can be observed in column 2, comes from the errors inherent in carrying out the experiments performed to determine the values of η_i and S.

CONCLUSIONS

Verification of the Imura-Okano model indicates that it can be successfully applied for correlating the viscosity coefficients of nematic liquid crystals with the alignment parameter S. Nevertheless, as suggested in the present paper, a way of relating these quantities based

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

TABLE III

Straight-line equations for the function $\Delta\eta_i = f(S)$. $\Delta\eta_i = \eta_i/\eta_{iso} - 1$, (i = 1, 2, 3)

Compound	(1)Straight-line equation	(2)Intersection point $\Delta\eta_i$ ($S = 0$)	(3)Correlation coeff.
5CB	$\Delta\eta_1 = 1.03$ S	− 0.01	0.990
	$\Delta\eta_2 = 0.62$S	0.002	0.998
	$\Delta\eta_3 = 0.42$ S	0.007	0.980
8CB	$\Delta\eta_1 = 1.69$ S	0.015	0.990
	$\Delta\eta_2 = 0.08$ S	0.001	0.999
	$\Delta\eta_3 = 0.55$S	0.012	0.970

on the analogies with anisotropy of other physical parameters gives a more accurate relationship. This fact has been proved by higher values of the correlation coefficients obtained for the experimental data.

Downloaded by [Tomsk State University of Control Systems and Radio] at 14:24 19 February 2013

Acknowledgment

The author wishes to express his grateful appreciation to Dr. M. Jawdosiuk of the Institute of Organic Chemistry and Technology, Warsaw Technical University, for carrying out the syntheses of the investigated substances.

References

1. M. Mięsowicz, *Nature*, **136**, 261 (1935).
2. Ch. Gähwiller, *Mol. Cryst. Liq. Cryst.*, **7**, 153 (1969).
3. J. W. Summerford et al., *J. Appl. Phys.*, **46**, 970 (1975).
4. W. H. de Jeu, *Phys. Lett.*, **69A**, 122 (1978).
5. H. Kneppe and P. Schnelder, *Mol. Cryst. Liq. Cryst.*, **65**, 23 (1981).
6. N. J. Koshkin and S. V. Čumakova, *Kristallografia*, **23(2)**, 432 (1978).
7. K. Skarp et al., *Mol. Cryst. Liq. Cryst.*, **60**, 215 (1980).
8. L. Leger and A. Martinet, *J. Phys.* (Paris), C-3, **37**, 89 (1976).
9. H. Kneppe et al., *Ber. Buns. Gesells. Gesells. phys. Chemie*, **85**, 784 (1981).
10. J. L. Ericsen, *Trans. Soc. Rheol.*, **5**, 23 (1961).
11. J. L. Ericsen, *Arch. Rat. Mech. Analysis*, **9(1)**, 26 (1962).
12. F. M. Leslie, *Arch. Rat. Mech. Analysis*, **28(4)**, 264 (1968).
13. F. M. Leslie, *Rheol. Acta*, **10**, 91 (1971).
14. F. M. Leslie, *Adv. Liq. Cryst.*, AP, NY, Vol. 4, 1979.
15. P. Parodi, *J. Phys.* (Paris), **31**, 581 (1970).
16. H. Imura and K. Okano, *Jap. J. App. Phys.*, **11(10)**, 1440 (1972).
17. G. Horn, *J. Physique*, **39**, 105 (1978).
18. J. W. Baran et al., *Bull. de l'Acad. Polon. Scie., Ser. sci. Chim.*, **26(2)**, 117 (1979).
19. D. A. Dunmur and W. H. Miller, *J. Physique*, C3, **40(4)**, 141 (1979).
20. S. Kobinata et al., *Mol. Cryst. Liq. Cryst.*, **66**, 67 (1981).
21. K. Miyano, *J. Chem. Phys.*, **69(11)**, 4807 (1979).
22. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976).
23. L. M. Blinov, Elektro-i magnitooptika źidkich kristallov, Nauka, Moskva, 1978.