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The Viscosity-Pressure Behavior of Three 4-Trans-(4-Alkyl)-Cyclohexyl-Benzonitriles and of an Eutectic Mixture

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The Viscosity-Pressure Behavior of Three 4-Trans-(4-Alkyl)-Cyclohexyl-Benzonitriles and of an Eutectic Mixture

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The viscosity of the title substances (with alkyl = C_3H_7, C_5H_{11}, C_7H_{15}) was measured at 6–7 temperatures up to 2 kbar. The results are interpreted onhand of pVT-data published earlier.

The compressibility and the viscosity as functions of *density* raise the indication of an anisotropic compressibility. Furthermore the activation energies E_p and E_V are determined. The ratio E_p/E_V shows an unusual behavior. In the isotropic range it decreases from relative high values like 5 to about 2 just before the transition isotropic/nematic. It gets the value 1 direct behind the transition and a value of about 1.6 in the proximity of the nematic/solid transition.

I. INTRODUCTION

In a preceding paper[1] the *pVT-Data* for the four substances mentioned in the title were investigated. Using the Tait-Equation for the representation of the measured values, the following results were obtained:

(a) For the *isotropic range* the Tait-Equation with only two constants B and C is more suitable than several other equations. C is independent of temperature and chain-length of the molecule, whereas the constant B depends systematically on both.

(b) For the *nematic range* the Tait-Equation has to be modified. The original constant C increases with increasing temperature and decreases with the chain-length.

(c) The *compressibility* is greater in the ordered nematic phase directly after the transition point than in the isotropic phase just before transition.

In this paper the viscosity-pressure behavior of the same compounds is investigated and interpreted onhand of the pVT-data. Only the knowledge of pVT- and viscosity-pressure-data makes it possible, to separate the real influences of temperature and density on viscosity. This may be of interest, since the temperature-dependence of a physical property at atmospheric pressure is caused by a superimposition of two effects:

(1) the real dependence on temperature and

(2) the additional influence of the density, changed simultaneously with temperature. In many cases the second effect is dominating.

Furthermore it may be tested, if the simple exponential law $\eta_p = \eta_o \exp(\alpha p)$ is valid in the nematic as well in the isotropic phase. Of special interest is the behavior of the viscosity-pressure coefficient α in the proximity of the transition point.

Finally, the heat of activation E_p and the energy of activation E_V for the viscous flow, characteristic for the structure of the liquid, can be determined making use of the $\eta - p$ and the pVT-data.

II. THE HIGH-PRESSURE VISCOMETER

Experiments were performed along 6–8 isotherms in the pressure range of 1–2000 bars and temperature range of 25–200°C on both sides of the nematic–isotropic transition.

With regard to temperatures above 100°C the pressure-autoclave was equipped with a closed casing, through which oil of the desired temperature was pumped. The seals of the pressure vessel were made of Teflon/Glass and in order to record the running time of the ball, a capacitive method was developed in place of the inductive method. The circuit diagram is described in an earlier paper.[2]

The reproducibility of the measurements was better than 1 percent. The substances and their structure are the same as described in an earlier paper.[1]

III. EXPERIMENTAL RESULTS

The viscosities measured for the four substances are given in Tables I–IV as a function of pressure and temperature. Above the horizontal

TABLE I

Trans-4-propyl-(4-cyanophenyl)-cyclohexane. Merck Licristal S 1103 PCH

	Viscosity in mPas						
bar	60	70	80	90	100	110	120°C
1	6.44	4.95	3.92	3.20	2.68	2.29	1.99
100	7.38	5.65	4.46	3.63	3.03	2.58	2.23
200	8.44	6.44	5.07	4.11	3.42	2.90	2.50
300	8.96	7.32	5.74	4.64	3.84	3.26	2.79
400	7.14	8.31	6.48	5.22	4.31	3.64	3.11
500	7.85	9.41	7.34	5.84	4.83	4.07	3.45
600	8.64	6.97	8.29	6.55	5.39	4.53	3.83
700	9.64	7.59	9.32	7.32	6.00	5.03	4.23
800	10.77	8.38	6.85	8.17	6.67	5.57	4.67
900	12.18	9.18	7.39	9.09	7.39	6.15	5.13
1000	13.71	10.12	8.04	6.94	8.17	6.78	5.64
1100	—	11.23	8.76	7.06	9.02	7.45	6.18
1200		12.52	9.58	7.61	8.56	8.17	6.76
1300		14.06	10.56	8.22	7.04	8.93	7.37
1400		15.77	11.68	9.01	7.51	9.76	8.03
1500			12.99	9.92	8.06	7.33	8.72
1600			14.44	10.97	8.81	7.45	9.46
1700			16.13	12.08	9.61	7.95	10.26
1800			—	13.22	10.50	8.59	7.43
1900				14.74	11.42	9.33	7.82
2000				16.29	12.49	10.11	8.33

lines the substances are in the isotropic phase and below them in the nematic phase.

The transition region is investigated by many measuring points, which can not be given in the tables.

However, in Figure 1 the general behavior and the course in the proximity of the transition point are shown by using Trans-4-Heptyl-(4-cyanophenyl)-Cyclohexane, S 1115 PCH Merck, as an example.

From this the following features may be recognized:

(1) In the *isotropic range* of the semi-logarithmic diagram the isotherms are almost linear with a small decrease in the gradient at higher pressures. Therefore the extended equation

$$\eta_p = \eta_o \exp(\alpha p + \beta p^2)$$

is used for the representation of the isotherms in place of the simple exponential form given above.

The constants α and β were determined by computer evaluation from the experimental values. They are tabulated for the isotropic range together with other characteristic data in Table V. It can be seen,

TABLE II

Trans-4-pentyl-(4-cyanophenyl)-cyclohexane. Merck Licristal S 1114 PCH

	Viscosity in mPas							
bar	60	70	80	90	100	110	120	130°C
1	9.03	6.79	5.26	4.18	3.40	2.83	2.41	2.08
100	10.44	7.84	6.01	4.77	3.86	3.22	2.72	2.34
200	7.89	8.98	6.85	5.41	4.37	3.63	3.07	2.64
300	8.53	10.23	7.74	6.11	4.93	4.08	3.46	2.96
400	9.35	7.89	8.75	6.89	5.55	4.59	3.87	3.31
500	10.29	8.38	9.83	7.73	6.22	5.14	4.33	3.69
600	11.43	9.16	8.02	8.67	6.96	5.75	4.82	4.11
700	12.81	10.07	8.16	9.70	7.76	6.39	5.37	4.56
800	—	11.07	8.81	10.83	8.65	7.11	5.96	5.06
900		12.20	9.55	8.08	9.62	7.89	6.60	5.59
1000		13.48	10.40	8.56	10.67	8.72	7.28	6.15
1100		14.92	11.36	9.16	8.55	9.63	8.02	6.76
1200		16.55	12.45	9.85	8.30	10.60	8.80	7.41
1300		18.42	13.67	10.64	8.91	—	9.63	8.12
1400		20.54	15.04	11.56	9.62	8.51	10.49	8.84
1500		22.97	16.57	12.60	10.40	9.09	11.38	9.59
1600		—	18.30	13.76	11.28	9.75	9.26	10.38
1700			20.27	15.12	12.30	10.51	9.17	11.23
1800			22.51	16.67	13.48	11.42	9.91	12.11
1900			25.06	18.52	14.94	12.59	10.87	9.58
2000			—	20.79	16.75	14.08	12.09	—

that the pressure coefficient α increases slightly with longer chain-length and decreases with increasing temperature.

(2) At the isotropic/nematic transition the viscosity decreases by about 25 percent, whereas the density increases by $\Delta\rho = 0.0054$ g/ml, i.e. by about 0.58 percent.

Increasing density normally effects an increase in the viscosity. The overcompensation, that manifests itself as a sharp decrease in viscosity, is caused by the realignment of the molecules into parallel arrangements.

(3) After the transition the viscosity passes through a flat minimum, beyond this the rate of increase is greater than exponential. This can be seen from the curved isotherms of Figure 1. Thus the Barus Equation can not be applied in the nematic range.

IV. INTERPRETATIONS

(a) The diagram lg $\eta = f(\rho)$

Since the pVT- and the viscosity-pressure data are now known, the log η — isotherms of the substances can be drawn as a function of the

TABLE III

Trans-4-heptyl-(4-cyanophenyl)-cyclohexane. Merck Licristal S 1115 PCH

	Viscosity in mPas						
bar	50	60	70	80	90	100	110°C
1	8.97	11.16	8.29	6.39	5.09	4.19	3.52
100	10.12	8.36	9.46	7.26	5.76	4.73	3.95
200	11.40	9.02	10.80	8.25	6.52	5.33	4.42
300	12.87	9.77	9.06	9.36	7.35	5.97	4.93
400	14.53	10.69	8.81	10.61	8.27	6.68	5.49
500	16.44	11.78	9.47	11.98	9.27	7.43	6.08
600	18.60	13.06	10.24	8.80	10.42	8.31	6.76
700	21.14	14.59	11.23	9.25	11.68	9.21	7.40
800	24.10	16.39	12.35	9.90	9.58	10.28	8.23
900	27.54	18.46	13.57	10.64	9.23	11.45	9.09
1000	31.51	20.80	14.96	11.48	9.60	12.69	10.02
1100	—	23.47	16.54	12.46	10.11	9.59	11.03
1200		26.49	18.32	13.57	10.83	9.57	12.10
1300		29.90	20.31	14.78	11.62	9.85	13.23
1400		33.75	22.53	16.14	12.49	10.43	9.81
1500		—	25.03	17.68	13.43	11.08	9.84
1600			27.85	19.38	14.51	11.79	10.14
1700			31.02	21.27	15.71	12.56	10.66
1800			34.59	23.36	17.05	13.42	11.24
1900			—	25.73	18.53	14.35	11.87
2000				28.37	20.15	15.34	12.53

density, which characterizes the average distances between the molecules.

The distances between the molecules are decisive for the interacting forces. Thus pressure is merely used, to vary the intermolecular distances within relatively wide limits without having to change the temperature. Figure 2 shows lg η vs ρ for S 1114.

In the isotropic range lg η increases almost linearly with increasing density. However, in the nematic range, after the decrease in viscosity (not shown in diagram), the isotherms bend in a convex manner to the density axis and the viscosities are much lower than those which would be expected for an isotropic phase with corresponding density.

This viscosity behavior may be compared with the reciprocal of the compressibility κ, which is reproduced in Figure 3 as function of density.

Usually the compressibility of a liquid at atmospheric or at a fixed higher pressure increases with increasing temperature. In contrast to this the compressibility shows a striking *decrease* with increasing temperatures, if it is observed at equal densities.

Indeed it can be seen from Figure 3, that the *reciprocal of* κ in the isotropic range increases almost linearly with increasing density and

TABLE IV

The eutectic mixture of 30% (S 1103) + 40% (S 1114) + 30% (S 1115).
Merck Licristal NP 1083

	Viscosity in mPas.			
bar	60	80	100	120°C
1	8.43	5.31	3.72	2.76
100	9.82	6.09	4.20	3.07
200	11.41	6.97	4.73	3.43
300	8.75	7.94	5.31	3.81
400	9.57	9.02	5.95	4.22
500	10.48	10.23	6.65	4.68
600	11.56	11.57	7.42	5.18
700	12.88	(11.10)	8.24	5.71
800	14.55	9.82	9.16	6.30
900	—	10.61	10.17	6.93
1000		11.50	11.31	7.60
1100		12.56	12.58	8.32
1200		13.84	(10.87)	9.10
1300		15.18	10.39	9.96
1400		—	11.14	10.88
1500			12.06	11.95
1600			13.04	12.98
1700			14.12	14.41
1800			15.32	(11.43)
1900			—	11.77
2000				12.58

with increasing temperature. However, the isotherms in the *nematic* range lie close together. Even if the ρ-scale is triplicated, a temperature dependence of $1/\kappa$ is not discernible.

In the same sense the relationship between lg η and $1/\kappa$ is modified too. In the nematic range lg η increases with growing $1/\kappa$ much less than in the isotropic range. Thereby it should be taken into account, that according A. E. White, P. E. Cladis and S. Torza[3] the apparent viscosity under the conditions of our measurements should be nearly the Miesowics viscosity η_2 belonging to molecules arranged with the long axis in the direction of flow. Only in direct proximity of the transition point the apparent viscosity additionally should be influenced also by η_1.

Apparently the compressibility and the viscosity-pressure dependence indicate, that at a fixed density the mutual forces in the direction perpendicular to the longitudinal axis of the molecules are much weaker than those in longitudinal direction.

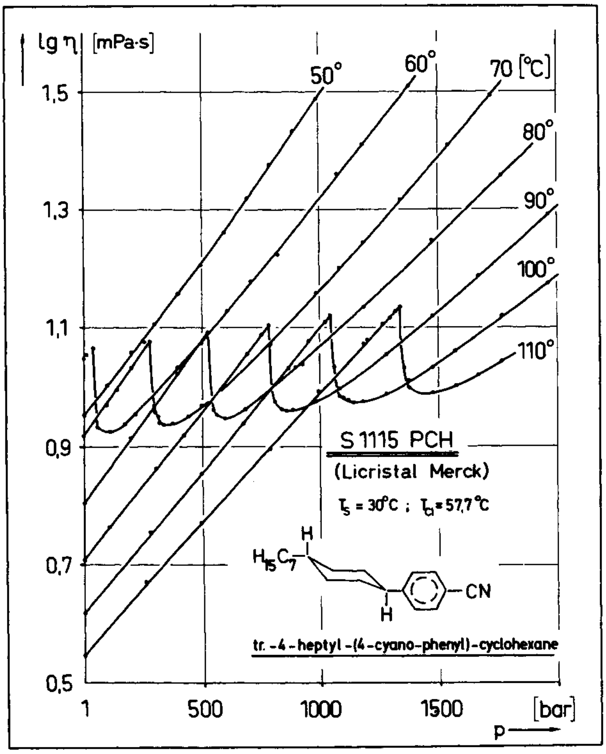

FIGURE 1 The viscosity-pressure isotherms of S 1115 PCH (Licristal Merck).

In our opinion the cause for the existence of the nematic phase is the *anisotropy of polarizability* of the single molecule. The polarizability itself is decisive for the intermolecular forces and the very high polarizability in the longitudinal direction of the molecule produces strong forces in this direction. Consequently at the transition isotropic/nematic the molecules move close together in the longitudinal direction of the molecules and the distances perpendicular to this direction become greater than before. In the nematic phase of strongly polar compounds a bilayer arrangement with strong antiparallel ordering of the molecules arises, as was found by J. E. Lydon and C. J. Coakley.[4]

The consequences of the described reorientation of the molecules should be:

(1) The dynamic viscosity η will strongly be diminished at the transition isotropic/nematic,

TABLE V

The matter-constants for viscosity-pressure behavior and for the compressibility of the substances in the isotropic range

	60	70	80	90	100	110	120°C
S 1103							
$\alpha\cdot10^3$	1.38	1.34	1.31	1.27	1.24	1.21	1.17
$\beta\cdot10^7$	−1.47	−1.39	−1.34	−1.30	−1.25	−1.20	−1.16
η_o	6.44	4.95	3.92	3.20	2.68	2.29	1.99
ρ_o	945.3	938.6	932.1	925.7	919.4	913.0	906.6
$\kappa_o\cdot10^6$	66.3	68.3	70.5	72.8	—	—	—
S 1114							
$\alpha\cdot10^3$	1.47	1.40	1.34	1.31	1.28	1.26	1.24
$\beta\cdot10^7$	−1.52	−1.48	−1.46	−1.42	−1.35	−1.32	−1.28
η_o	9.03	6.79	5.26	4.18	3.40	2.83	2.41
ρ_o	932.3	925.6	919.0	912.5	906.0	899.6	893.5
$\kappa_o\cdot10^6$	67.1	69.1	71.2	73.5	—	—	—
S 1115							
$\alpha\cdot10^3$	—	1.36	1.32	1.29	1.25	1.19	1.15
$\beta\cdot10^7$	—	−1.54	−1.50	−1.47	−1.40	−1.34	−1.29
η_o	—	8.29	6.39	5.09	4.19	3.52	3.03
ρ_o	921.5	914.2	907.0	899.9	894.1	888.0	882.0
$\kappa_o\cdot10^6$	67.9	70.1	72.3	74.8	—	—	—
NP 1083							
$\alpha\cdot10^3$	1.52	1.46	1.38	1.30	1.23	1.18	1.14
$\beta\cdot10^7$	−1.55	−1.49	−1.42	−1.35	−1.28	−1.23	−1.16
η_o	8.44	6.62	5.34	4.43	3.74	3.20	2.77
ρ_o	932.5	925.6	919.3	912.9	906.5	900.3	894.2
$\kappa_o\cdot10^6$	67.4	69.6	71.7	74.0	—	—	—

(2) The compressibility is increased at the transition-point, and

(3) presumably the compressibility will be *anisotropic* in the nematic phase.

The latter assumption will be encouraged by a paper of D. Guillon, P. E. Cladis, D. Aadsen and W. Daniels.[5] Interpreting X-ray measurements on CBOOA they came to the conclusion of an anisotropic compressibility, however not for a nematic phase but for the smectic-A-phase before transition to the solid state.

It may also be admitted, that high pressure work on single crystals has shown, that the compressibility of a zinc single-crystal in one direction is seven times greater than in the direction perpendicular to this[6] and that the differences for cadmium are even still stronger.[7] Also the synthesis of diamonds at 2800 K and 65 kbar is facilitated by the anisotropic high compressibility of the c-axis of graphite in comparison to

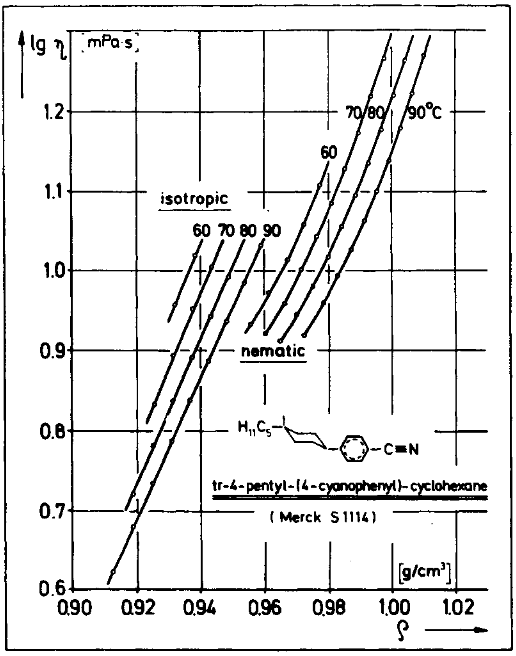

FIGURE 2 The viscosity of S 1114 in dependence on density.

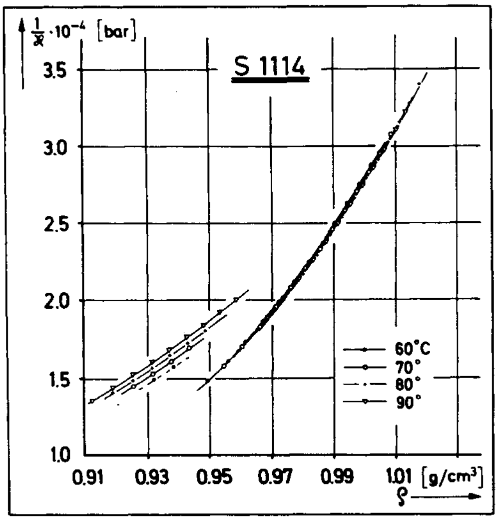

FIGURE 3 The reciprocal of the compressibility in dependence on the density.

the other axis. Atoms of the catalyst invade between the layers and form at a favorable distance with the π-orbital of the graphite sandwich-structures with the sp^3-electron-configuration of diamond.[8]

(b) The course of the isochors lg $(\eta)_V = f(1/T)$

The viscosity-temperature dependence at 1 bar or a fixed higher pressure is complicated, because simultaneously with the temperature also the density is changed and two effects are superimposed each other. By including the measured pVT-data and drawing *isochors* instead of isobars the two effects of temperature and density can be separated from another.

At simple liquids and even at mineral oils with their complicated structure we found, that the isochors lg η_V vs $1/T$ are almost linear in contrast to the pronounced bending of the lg η — ρ isotherms.[9] Therefore the corresponding diagrams for the liquid crystals S 1103 and S 1114 are given in Figure 4.

Indeed the isochors are linear even in the nematic range as well as in the isotropic phase and additionally they are showing nearly the same gradient. Only shortly after the transition the course of the isochors

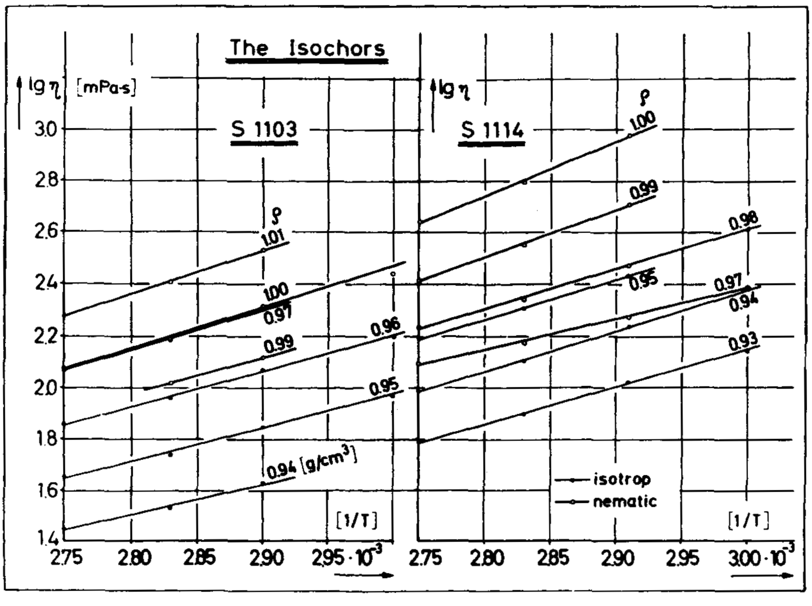

FIGURE 4 The isochors lg η_V as function of $1/T$.

becomes somewhat flatter, as can be seen from the nematic isochor 0.97 of S 1114. Regarding isochors of the same density for S 1103 and S 1114 we see furthermore, that the viscosity itself and the slope of the isochors are enhanced a little to higher chain-length.

Thus for the isochors the simple relation:

$$(\eta)_V = A \exp(B/T)$$

are valid in both phases and the true influence of temperature can be recognized.

As numerical values we find in

	the isotropic	the nematic range
A (mPa·s)	0.18 . . . 0.12	0.14 . . . 0.04
B (degrees)	1200 . . . 1600	1450 . . . 2200

ranged with increasing density.

(c) Interpretation using the Van Wijk-Seeder theory

Extending the kinetic theory of gases the Enskog-Chapman theory comprehends the following additional phenomena:[10,11]

(1) For a central collision the sudden transfer of impulse across the diameter of the pushed molecule,

(2) The unhomogeneous distribution of molecules in space,

(3) In the velocity distribution after the collision a certain preference for the velocity direction before collision. (Persistence of velocity).

The Enskog-Chapman equation for the viscosity of compressed gases contains an absolute, a linear and a quadratic term of density.

According to Van Wijk and Seeder[12] only the quadratic term is decisive for the viscosity in the closely packed liquid state. By introducing the Boltzman factor derived from the molecular distribution function, Van Wijk and Seeder obtain the final equation:

$$\frac{1}{\eta V} = \frac{V - b}{C} \exp(-B/RT)$$

In this C is a constant, V the molar volume, b the volume of the molecule and B a structure energy given by $B = E(r_o) - E(r)$. Since r_o relates to an ideal homogenous molecular distribution and r gives the actual distances between the molecules, B characterizes the structure of the liquid.

Converting this last equation into the logarithmic form we see, that B can be determined by plotting the lg *η-isochores* against $1/T$. Assuming, that C,b and the molecular weight M are independent of temperature linear curves are to be expected, the gradient of which would be the ratio B/R.

In Figure 4 it was already shown, that the isochors are linear in the isotropic and the nematic range. From there we obtain:

B isotropic	10 . . . . 13.5 kJ/mole	(2.4–3.2 kcal/mole)
nematic	12.2 . . . 18.6 kJ/mole	(2.9–4.4 kcal/mole)

increasing with density, however almost independent of temperature with the exception of the proximity of the transition point.

B of the liquid crystals is greater than that of ethanol (10.5 kJ/mole), however it is smaller than that of some mineral oils (10–60 kJ/mole).[9]

(d) Energies of activation for viscous flow

The various liquid state theories—like that of D. C. Andrade,[13] H. Eyring and others,[14,15] A. K. Doolittle,[16] M. H. Cohen and D. Turnbull[17] *et al.*—give more or less complicated relationships between viscosity and density. Most of these relationships include an exponential term in the form $\exp(E/RT)$.

According to the interpretation by Eyring *et al.*, E is the energy needed for the molecule to overcome the attractive forces by which it is held in position by the neighboring molecules and to jump into an empty site nearby. E_A is called the activation energy for viscous flow.

Since the other physical dimensions in the relation

$$\eta = 1.09\cdot 10^{-3}\,\frac{M^{1/2}T^{3/2}}{V^{2/3}U_V}\exp(E_A/RT)$$

vary only slightly with p and T compared with the viscosity, at a first approximation the exponential factor is decisive and the activation energy can be determined by:

$$E_p = R\left(\frac{\partial(\ln\eta)}{\partial(1/T)}\right)_p$$

Here the dependence of viscosity on temperature is observed at constant pressure. In an analogous manner the activation energy at constant volume:

$$E_V = R\left(\frac{\partial(\ln\eta)}{\partial(1/T)}\right)_V$$

can also be determined, which is more important than the activation heat E_p, because it indicates the sole influence of temperature without a superimposed influence of density.

In Figure 5 $E_p = f(p)$ is given for S 1115. Normally E_p increases with increasing pressure. However, in the proximity of the transition isotropic/nematic E_p falls off abruptly and subsequently in the nematic range it increases with pressure to values considerably higher than those of the isotropic phase.

On principle E_V can be obtained from the slope of the isochors in Figure 4. However, E_V can be evaluated more exactly from E_p with the thermodynamic equation:

$$E_V = E_p - RT^2\left(\frac{\partial p}{\partial T}\right)_V \cdot \alpha^*_{\text{visc.}}$$

In this α^* is the instantaneous gradient of the lg $\eta - p$ isotherms in Figure 1. Because of the bending of these isotherms we have replaced the simple Barus relation by the modified equation:

$$\eta_p = \eta_o \exp(\alpha p + \beta p^2)$$

From this relation α^* in the isotropic range can easily calculated with $\alpha^* = \alpha + \beta p$ using α and β from Table V, whereas α^* in the nematic range is determined graphically.

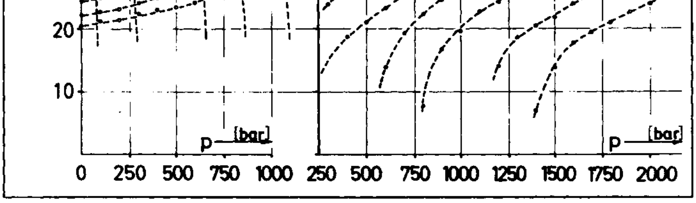

FIGURE 5 The activation energy E_p as function of pressure.

Furthermore we need for the evaluation of E_V the value $(dp/dT)_V$ which is the essential part in the well-known relation for the internal pressure:

$$p_i = T\left(\frac{\partial p}{\partial T}\right)_V - p_a$$

$(dp/dT)_V$ is obtained by the p-T isochors given in Figure 6 for S 1103 and S 1115. The rectilinear isochors yield for the nematic phase a somewhat greater gradient than for the isotropic range. Introducing α^* and the gradient $(dp/dT)_V$ in the thermodynamic relation mentioned above $E_V = f(p)$ is obtained, which is reproduced for S 1115 in Figure 7. Comparing Figure 5 and Figure 7 we see, that the courses of E_V and E_p are similar, however E_V is much smaller than E_p. Furthermore the temperature dependence is remarkably greater in the nematic range than in the isotropic range.

The difference between E_p and E_V can easily be recognized from the last term of the thermodynamic relation. In this $T(dp/dT)_V = p_i + p_a$ and $RT\,\alpha^*_{\text{visc}} = \Delta V$. Thus the last term of the relation is the energy necessary to form a hole of the volume ΔV, in which the molecule jumps at viscous flowing. ΔV is small for simple molecules and great for molecules with a high degree of molecular branching, as was shown in earlier papers.[18,19]

Since E_p would be the total energy to jump over a potential barrier and to form a hole and E_V is only the former part, $(E_p/E_V) - 1$ would

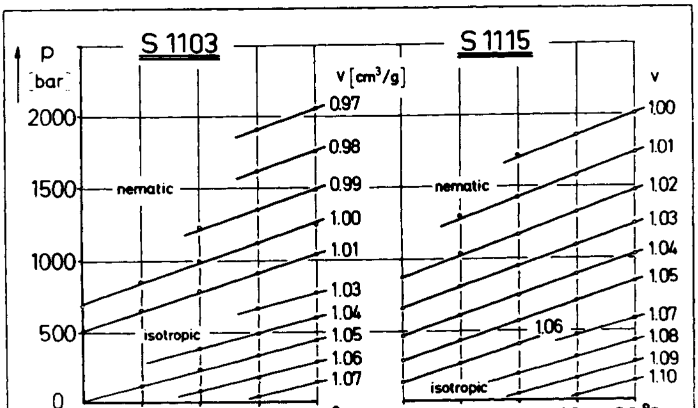

FIGURE 6 The p-T isochors needed for the evaluation of E_V.

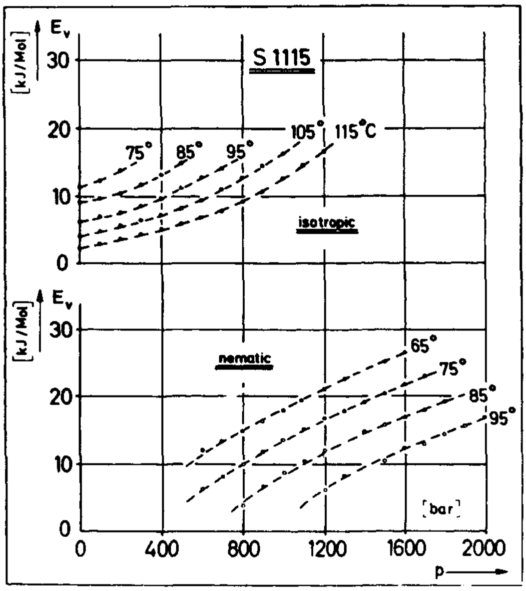

FIGURE 7 The activation energy E_V as function of pressure.

be the ratio of the hole formation energy to the high of the potential wall. This is of interest, because for many liquids E_p/E_V is approximately equal two.

However, this is not the case for liquid crystals. As example the values for S 1115 are collected in Table VI. The following results were obtained:

(a) E_p and E_V both increase with increasing pressure and decrease at higher temperatures. However, by elevating the pressure by about 400–700 bar depending of the temperature the initial value of E_V can be doubled, whereas E_p increases by only 20–30 percent.

(b) Therefore the ratio E_p/E_V is changed strongly with pressure. In the isotropic range near the isotropic/nematic transition E_p/E_V is almost equal to 2, but far away from the transition point (e.g. at 1 bar and 105°C for S 1115), where the transition occurs only at high pressure, E_p/E_V can be as high as 5.

(c) In the nematic range short after the transition no values are given in Table VI, since there is no sufficient accuracy. However, valuable information is given for this region by the thermodynamic relation given above. Since there occurs the viscosity minimum with $\alpha^*_{visc} = 0$, the equation demands $E_V = E_p$ or $E_p/E_V = 1$. This means, the hole forma-

TABLE VI

The activation-energies of Tr.-4-heptyl-(4-cyanophenyl)-cyclohexane

S 1115 PCH, Licristal Merck; Energies in kJ/mol

	65°			75°			85°			95°			105°C		
bar	E_p	E_V	E_p/E_V	E_p	E_V	E_p/E_V	E_p	E_V	E_p/E_V	E_p	E_V	E_p/E_V	E_p	E_V	E_p/E_V
1	28.4	14.1	2.01	26.3	11.6	2.27	24.4	9.23	2.64	22.2	6.22	3.57	20.3	4.05	5.01
100	—	—	—	26.8	12.4	2.16	24.9	9.94	2.50	22.7	7.03	3.23	21.0	4.97	4.22
200	—	—	—	27.4	13.0	2.11	25.5	10.5	2.43	23.2	7.62	3.04	21.5	5.71	3.76
300	16.3	(3.3)	(4.9)	—	—	—	26.6	11.8	2.25	24.0	8.65	2.77	22.1	6.54	3.37
400	18.6	6.7	2.78	—	—	—	27.9	13.3	2.09	24.9	9.79	2.54	22.7	7.39	3.07
500	20.9	9.2	2.27	—	—	—	29.1	14.8	1.96	26.1	11.2	2.32	23.4	8.33	2.81
600	23.2	11.1	2.09	14.0	6.14	—	—	—	—	27.3	12.8	2.13	24.2	9.38	2.58
700	25.3	13.2	1.92	19.2	8.12	2.36	—	—	—	28.5	14.2	2.01	25.6	11.0	2.32
800	27.0	14.9	1.81	22.2	9.99	2.22	7.9	(3.6)	(2.2)	—	—	—	27.0	12.7	2.12
900	29.3	16.8	1.74	24.4	11.7	2.08	16.6	6.7	2.48	—	—	—	28.6	14.6	1.96
1000	31.2	17.8	1.75	26.5	13.4	1.97	20.2	8.7	2.31	—	—	—	30.0	16.3	1.85
1100	33.2	19.3	1.72	28.4	15.1	1.89	22.6	10.3	2.19	—	—	—	—	—	—
1200	34.9	20.6	1.69	30.2	16.6	1.82	24.4	11.9	2.05	14.3	6.02	2.37	—	—	—
1300	36.7	21.9	1.67	31.9	17.6	1.81	25.9	13.3	1.95	18.6	8.79	2.11			
1400	38.3	23.5	1.63	33.6	19.0	1.76	26.6	13.6	1.82	20.4	9.50	2.16			
1500	39.8	25.0	1.59	34.9	20.2	1.73	29.3	15.7	1.86	22.1	10.3	2.14			
1600	41.4	26.3	1.57	36.5	21.6	1.69	30.7	16.7	1.84	23.9	11.5	2.07			
1700	—	—	—	37.9	22.9	1.66	32.2	17.9	1.80	25.5	12.6	2.02			
1800				39.4	24.2	1.63	33.6	19.1	1.76	27.3	14.1	1.93			
1900				40.8	25.5	1.60	35.0	20.3	1.72	28.9	15.4	1.88			
2000				42.4	27.0	1.57	36.4	21.6	1.68	30.6	16.9	1.81			

tion energy would be almost zero. This is in accordance with the picture given above and the assumption of an anisotropic compressibility.

(d) Finally as is shown in Table VI, E_p/E_V decreases also in the nematic range at higher pressures and attains almost the value 1.5 at the transition nematic/solid.

Till now only activation energies for the "twist viscosity" measured in a rotating magnetic field by several authors[20-25] at atmospheric pressure are known. These values (10.8–11.8 kcal/mole for MBBA resp. HBAB) have the same order of magnitude as our values at atmospheric pressure.

SUMMARY

The measured viscosity-pressure dependence of the title substances and the pVT data of the 4 substances published earlier were used, to separate the real influences of temperature and density. The following results were obtained:

(a) With the transition isotropic/nematic the viscosity is diminished by about 25 percent whereas the density is enhanced by about 0.58 percent.

(b) The compressibility κ *decreases* at constant density to higher temperatures. $1/\kappa$ increases linearly to higher temperatures, in the isotropic range. However in the nematic range the influence of temperature *disappears.* The slope of $\lg \eta$ as $f(1/\kappa)$ is smaller in the nematic than in the isotropic range.

(c) The $\lg \eta_V$-isochors as $f(1/T)$ enable the use of the Van Wijk-Seeder theory and the hole theories of the liquid state. The heat of activation E_p is given and by a thermodynamic relation also the energy of activation E_V is evaluated.

The *anisotropy of polarizability* is assumed as cause for the ordering of the molecules in the nematic phase. It produces a narrow arrangement in the longitudinal direction of the molecules and relatively wide distances and small intermolecular forces in the directions perpendicular to this. Therewith the viscosity is strongly diminished at the transition isotropic/nematic and the compressibility should be *anisotropic* in the nematic range.

The activation energies E_p and E_V are given in dependence of p and

T. An unusual behavior is found especially for E_p/E_V. In the isotropic range E_p/E_V decreases from relative high values like 5 down to a value about 2 just before the isotropic/nematic transition and gets the value 1 in the nematic phase directly after the isotropic/nematic transition. After a short increase E_p/E_V in the nematic phase is again decreasing with increasing pressures down to a value of about 1.6 in the proximity of the nematic/solid transition.

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