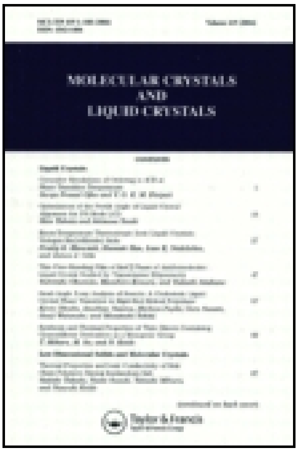

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Differential Thermal Analysis (DTA) and Dielectric Studies on 4-(Trans-4-Pentyl-Cyclohexyl)-Benzonitrile (PCH-5) Under High Pressure

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DIFFERENTIAL THERMAL ANALYSIS (DTA) AND DIELECTRIC STUDIES ON 4-(TRANS-4-PENTYL-CYCLOHEXYL)-BENZONITRILE (PCH-5) UNDER HIGH PRESSURE

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Abstract : The phase diagram of 4-(trans-4-pentyl-cyclohexyl)-benzonitrile, PCH-5, was obtained by DTA measurements up to a temperature of 370 K and up to pressures of 260 MPa. Dielectric studies on the static and complex permittivity have been performed on PCH-5 in the pressure range 0.1 - 140 MPa, the frequency range 1 kHz - 13 MHz and the temperature range 311 - 350 K. From the relaxation times in the nematic phase, $\tau_{\parallel}$, we have calculated the activation volume, $\Delta^{\ddagger}V_{\parallel}$, of about 70 cm³/mol (decreasing with increasing temperature), and the activation enthalpy, $\Delta^{\ddagger}H_{\parallel}$, of approximately 70 kJ/mol. The pressure dependence of $\Delta^{\ddagger}H_{\parallel}$ is weaker than that found recently for 5CB. We have also calculated the (isochoric) activation energy of about 40 kJ/mol. The low-frequency relaxation process connected with molecular rotations about the short molecular axis was analysed in terms of the Martin-Meier-Saupe theory, yielding $q \approx 10$ kJ/mol for the nematic potential. The results are compared with recent high pressure results on 4-n-alkyl-4'-cyanobiphenyls.

1. INTRODUCTION

Many liquid crystals (LCs) with a strong positive dielectric anisotropy in the nematic phase are of special interest because of their use in electrooptical devices. Because of these dielectric properties a large number of thermotropic LCs have been studied at atmospheric pressure [1,2]. On the other hand, investigations of these substances at high pressures are relatively scarce. However, our recent high pressure studies on several 4-n-alkyl-4'-cyanobiphenyls [3-7] and 6CHBT [8] have provided additional valuable information of the dielectric relaxation process. Now we start to investigate the alkyl-cyclohexyl-benzonitrile series, in order to check the influence of different molecular frames on the dielectric behaviour.

In particular we are concerned with the investigation of the low-frequency relaxation process connected with molecular reorientations about the short axis in the nematic phase. This motion is observed for the parallel orientation of the sample in the electric field. The rotations about the short molecular axes are strongly opposed by neighbouring molecules. To take into account this interaction *Maier* and *Saupe* introduced the nematic potential q [9].

2. EXPERIMENTAL

The experimental set-up for the DTA measurements as well as for the dielectric studies was the same as in previous studies and has been described for example in [10] and [11]. The measurements of the complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were performed in the frequency range 1 kHz to 13 MHz using a Hewlett Packard impedance analyzer (model HP 4192A). The conductivity contribution to the dielectric losses was fully subtracted. The capacitor and the high pressure vessel do not allow us to orient the sample by a magnetic field during the measurements. However, due to the very low conductivity of the sample ($G \simeq 0.1$ µS/m) we were able to apply a DC bias field $E \simeq 300$ V/cm. Because of the strong dipole moment directed along the symmetry axes of the molecules this field oriented the molecules of our sample parallely to the measuring field ($n \parallel E_{bias}$).

After filling the capacitor with the sample we carried out the measurements at atmospheric pressure in the temperature range covering the nematic and isotropic phase of PCH-5. The dielectric spectra under pressure were in general obtained by gradually decreasing the pressure at a constant temperature, after pressurizing the sample to 140 MPa or a point near the phase boundary to the solid state. To check the reliability of the results we repeated some runs at T = constant and at p ≃ constant. The reproducibility of the results was usually better than 2%.

3. RESULTS

3.1. Phase behaviour

The phase behaviour of PCH-5 at elevated pressures has been partly determined by *Kuss et al.* [12], without reporting the melting curve. However, the knowledge of the exact solid-nematic coexistence curve is important for our dielectric measurements, in order to avoid unwanted crystallization of the sample. Therefore the phase diagram of PCH-5 was established using high pressure differential thermal analysis [13]. The agreement between our data for the nematic-isotropic coexsistence curve and the data reported by *Kuss* is very good (see FIG.1).

The phase transition lines for PCH-5 can be represented by polynomials:

solid → nematic: $T(K) = 303.1 + 0.246 \cdot (p/MPa) - 1.09 \cdot 10^{-4} \cdot (p/MPa)^2$

nematic → isotrop: $T(K) = 328.1 + 0.440 \cdot (p/MPa) - 1.11 \cdot 10^{-4} \cdot (p/MPa)^2$

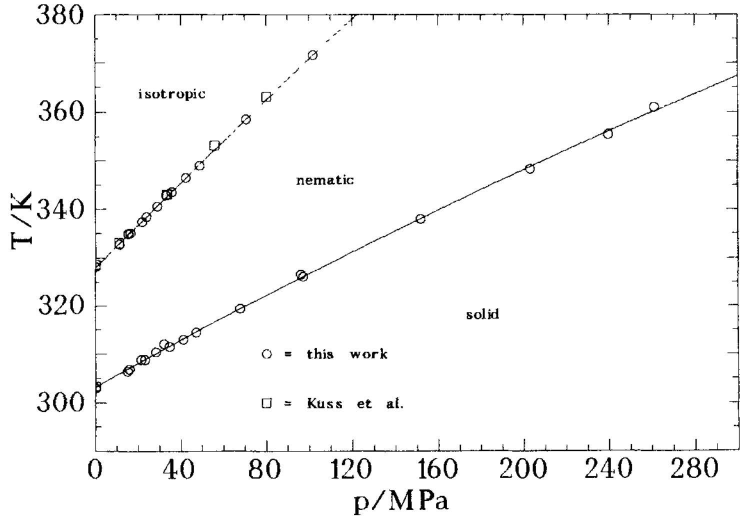

FIG.1 : Phase diagram of PCH-5.

The DTA peak areas have been calibrated against the solid-liquid transition of cyclohexane to obtain the enthalpy changes accompanying the phase transitions. Some thermodynamic data at normal pressure are compiled in TABLE 1. The volume changes have been calculated using the Clausius-Clapeyron equation. The agreement with the literature data is satisfactory.

TABLE 1 : Thermodynamic Properties of PCH-5 at 1 atm

transition	T/K	ΔH/kJ mol^{-1}	ΔV/cm^3 mol^{-1}	literature
solid → nematic	303.05	21.9	17.33	this work
"	303.15	21.353	-	MERCK [14]
nematic → isotrop	328.14	0.923	1.29	this work
"	328.05	0.963	-	MERCK [14]
"	328.15	-	1.30	Abdah [15]

3.2. Measurements at atmospheric pressure

FIG.2 shows the static permittivity, $\varepsilon_{0\parallel}$, measured at atmospheric pressure in comparison to the results obtained by MERCK [14] and *Sen et al.* [16]. In the nematic phase our results agree well with the results reported by MERCK; whereas relatively large differences are observed between our values and the data reported by *Sen et al.* for the nematic and isotropic phase.

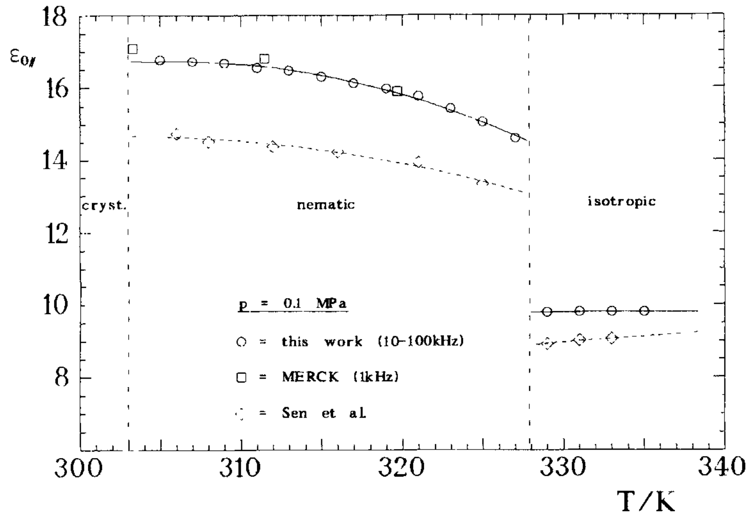

FIG.2 : Static permittivity as a function of temperature at atmospheric pressure.

We have measured the variation of the dielectric permittivity ε' and the dielectric loss factor ε'' as a function of the frequency of the measuring field at different temperatures in the nematic and isotropic phase of PCH-5. The maximum of the loss curves is shifted to higher frequencies with increasing temperature. The curves for the nematic and isotropic phase are clearly discernible. The loss curves for the nematic phase have been fitted to the Jonscher, Havriliak-Negami, Cole-Cole and Cole-Davidson equations. The Jonscher equation was preferred to calculate the dielectric relaxation time $\tau_{\parallel}$ from the frequency of maximum loss. The Cole-Cole plots demonstrate that in the nematic phase a single relaxation domain of the Debye-type is prevailing.

In the isotropic phase the low and high frequency processes merge to give one broad relaxation spectrum. Due to the frequency limit of our bridge (≤13 MHz) we could only measure part of the loss curve in the isotropic phase. Therefore, for further evaluations we used some data obtained at atmospheric pressure with the aid of time domain spectroscopy (TDS) up to frequencies of 1 GHz [17]. These results from TDS-method have shown that even in the isotropic phase the best fitting of the loss-curves is achieved by the use of the Cole-Cole equation.

3.3. Measurements at elevated pressures

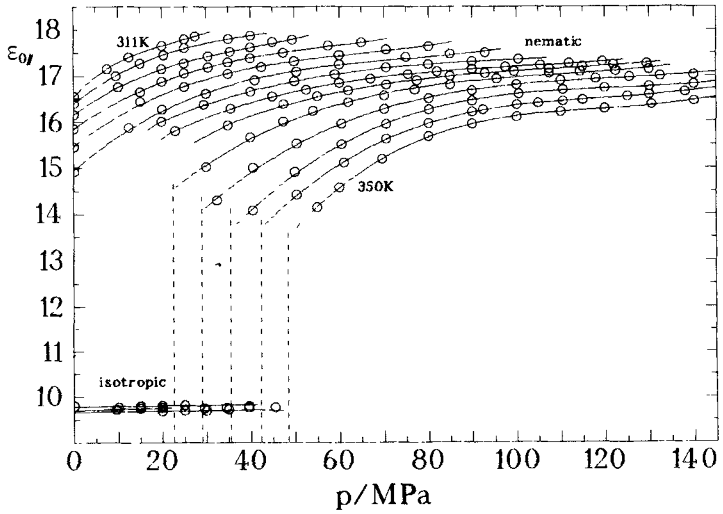

FIG.3 : Static permittivity as a function of pressure in the nematic and isotropic phase of PCH-5; the temperature for the different isotherms varies in steps of 3 K.

In FIG.3 the static permittivity, $\varepsilon_{o\parallel}$, is plotted as a function of pressure at different temperatures. On approaching the clearing temperature the permittivity decreased strongly and remained essentially constant in the isotropic phase. In FIG.4a we present some examples of the frequency dependence of the real and imaginary parts of the complex permittivity measured at different pressures in the nematic and isotropic phase of PCH-5.

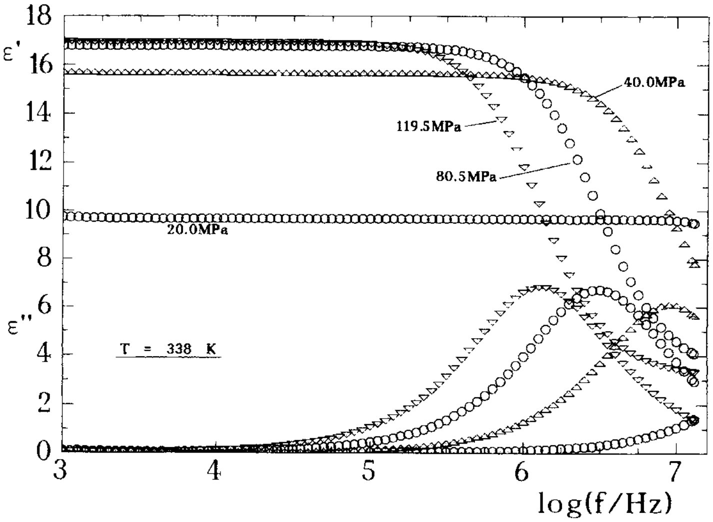

FIG.4a : Dielectric dispersion and absorption as a function of pressure at T = 338 K.

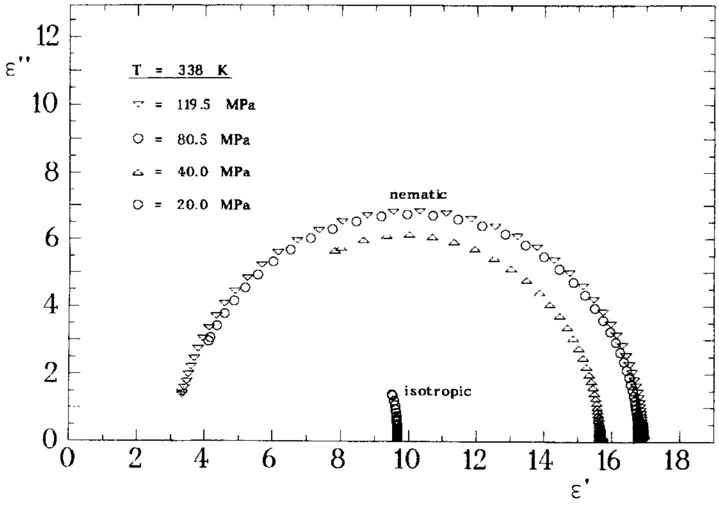

FIG.4b : Cole-Cole plots for different pressures at T = 338 K.

The maximum of the loss curves is shifted to higher frequencies with decreasing pressure. In the nematic phase the dielectric spectra obey a single Debye relaxation very well (see FIG.4b). The relaxation times $\tau_{\parallel}$ calculated with the use of the Jonscher equation for different pressures in the nematic and isotropic phase are presented in semi-logarithmic scale in FIG.5. In the nematic phase the relaxation times are not a strictly exponential function of the pressure, the $\ln\tau_{\parallel}$ versus p curves are a little bit bent, especially in the vicinity of the nematic-isotropic transition lines. Neglecting the points very close to these lines, we have calculated the slopes of the curves by means of linear regression. The figure shows also some plots for the isotropic phase which have been extrapolated beyond the phase boundary to the nematic phase in order to estimate τ_0-values which will be used to calculate the retardation factor (see below).

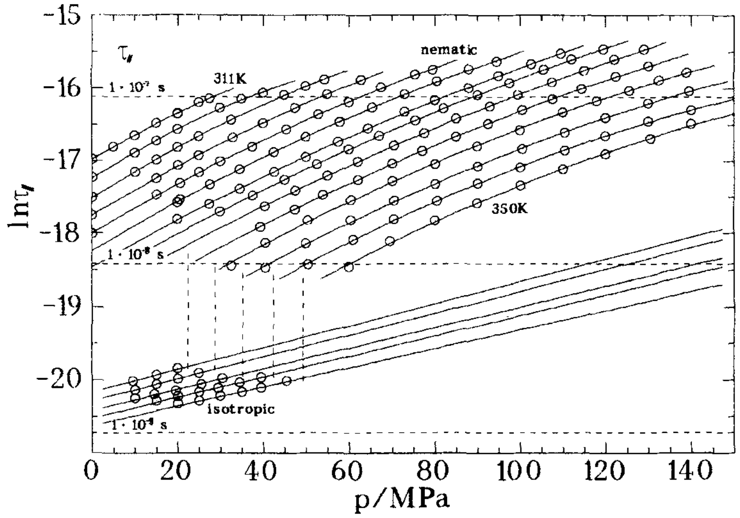

Fig.5 : Logarithm of the relaxation times as a function of pressure for different temperatures in the nematic and isotropic phase; the temperature for the different isotherms varies in steps of 3 K.

From the temperature and pressure dependence of the relaxation time $\tau_{\parallel}$ we have calculated the activation volume:

$$\Delta^{\ddagger}V_{\parallel} = R * T * (\partial\ln\tau_{\parallel}/\partial p)_T ,$$

of approximately 70 cm^3/mol, decreasing with increasing temperature, (see

FIG.6) and the activation enthalpy :

$$\Delta^{\ddagger}H_{\parallel} = R * (\partial \ln\tau_{\parallel}/\partial(1/T))_p ,$$

of about 70 kJ/mol, decreasing very little with increasing pressure, (see FIG.7).

We have used some p-V-T data from *Kuss et al.* [12], in order to calculate the (isochoric) activation energy :

$$\Delta^{\ddagger}U_{\parallel} = R * (\partial \ln\tau_{\parallel}/\partial(1/T))_{Vm} ,$$

of ≃ 40kJ/mol, decreasing with increasing molar volume (see FIG.8).

4. DISCUSSION

In FIG.6-8 we have plotted the activation quantities for PCH-5 and the corresponding data for 5CB. It can be seen that the $\Delta^{\ddagger}V_{\parallel}$- and $\Delta^{\ddagger}H_{\parallel}$-values are significantly higher for PCH-5. This relatively large difference cannot be explained by the different molar masses (M= 255.40 g/mol for PCH-5 and M= 249.35 g/mol for 5CB) of the substances. The higher activation volume for PCH-5 is probably connected with the higher flexibi-

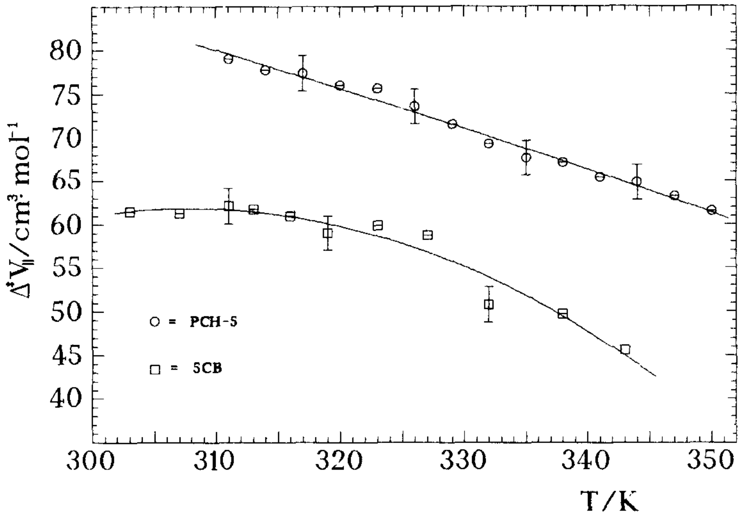

FIG.6 : Activation volume, $\Delta^{\ddagger}V_{\parallel}$, as a function of temperature.

lity of the cyclohexyl ring that requires more space for the reorientation process. The pressure dependence of the activation enthalpy is relatively weak in the case of PCH-5 (FIG.7). Its variation with pressure is nearly zero within the limits of experimental error. On the other hand 5CB shows a strong decrease of $\Delta^{\ddagger} H_{\parallel}$ with increasing pressure.

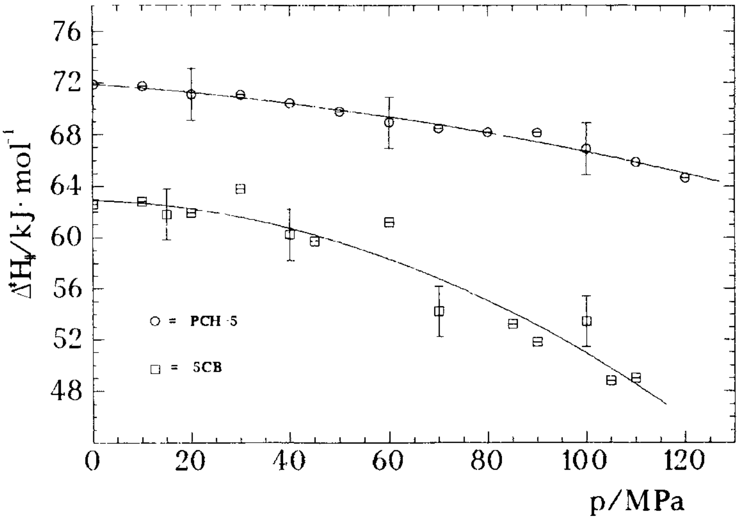

FIG.7 : Activation enthalpy, $\Delta^{\ddagger} H_{\parallel}$, as a function of pressure.

Even larger discrepancies are observed for the activation energy, $\Delta^{\ddagger} U_{\parallel}$, as a function of the molar volume. FIG.8 shows that PCH-5 and 5CB ex-

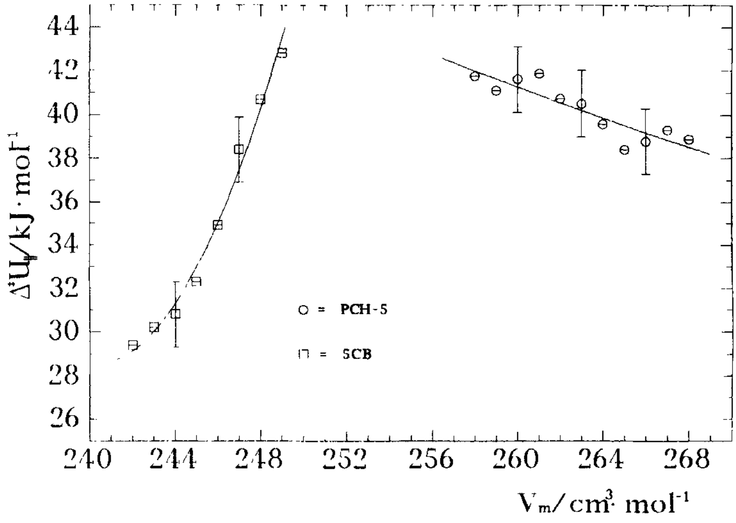

FIG.8 : Activation energy, $\Delta^{\ddagger} U_{\parallel}$, as a function of the molar volume.

hibit even different signs of the slopes in the $\Delta^{\ddagger}U_{\parallel}$ versus V_m plot. The decrease of $\Delta^{\ddagger}U_{\parallel}$ with increasing molar volume is also in general observed for plastic crystals [18], whereas for 5CB an opposite behaviour has been found [3]. In the case of 5CB and its homologues up to 8CB the peculiar pressure dependence has been discussed in the frame of a monomer-dimer equilibrium. Increasing pressure destroys more or less associates of antiparallel dimers thus reducing the activation enthalpy with pressure. Therefore it is open to question, whether for PCH-5 the same monomer-dimer equilibrium exists, although this was proposed in the literature [19,20].

Striking differences are also observed for the pressure dependence of the static permittivity. Both substances, PCH-5 and 5CB, have practically the same dipole moment, μ, of about 4.2 Debye. Therefore, in the isotropic phase of the two components the ε_o-values are comperable ($\varepsilon_o \approx 10$); whereas the values for $\varepsilon_{o\parallel}$ in the nematic phase are considerably different (for 5CB $\varepsilon_{o\parallel} \approx 20$, for PCH-5 $\varepsilon_{o\parallel} \approx 16$). For the 4-n-alkyl-4'-cyanobiphenyls $\varepsilon_{o\parallel}$ increases much more with rising pressure than for PCH-5. This increase can be interpreted as an increase of the *Kirkwood-g-factor* caused by the destruction of antiparallel dimers. For PCH-5 the pressure dependence of $\varepsilon_{o\parallel}$ is much less pronounced (FIG.3). Certainly the higher activation quantities as well as the weaker sensitivity on pressure of the activation parameters and $\varepsilon_{o\parallel}$ are caused by stronger dipole-dipole correlations in the nematic phase of PCH-5.

The low-frequency relaxation process about the short molecular axis was also analysed in terms of theories from *Martin*, *Meier* and *Saupe* [21]. They introduced so called retardation factors, $g_{\parallel}$, as ratios of the relaxation time, $\tau_{\parallel}$, in the nematic phase and τ_0 , being the relaxation time of a hypothetical state with a nematic potential $q = 0$. We have taken our measured pressure dependencies for τ_{iso} and connected them with the normal pressure values for τ_{iso}, measured by *Gestblom* and *Urban* [17], in order to get reliable data for the relaxation times in the isotropic phase at elevated pressures. τ_0 is obtained from an extrapolation of these τ_{iso}-values beyond the phase boundary to points corresponding to the nematic phase [6-8].

$$g_{\parallel} = \tau_{\parallel}/\tau_0 = (RT/q) [\exp (q/RT) - 1] .$$

This equation enables us to estimate the nematic potential as a function of temperature and pressure (see FIG.9), yielding $q \approx 10$ kJ/mol (decreasing with increasing temperature and with decreasing pressure).

This value for the nematic potential is distinctly higher than the corresponding value for 5CB, q ≈ 6 kJ/mol. Nevertheless the temperature and pressure dependencies are the same for both substances. The *Maier-Saupe-Theory* predicts a $g_{\parallel}$-factor of 4 at the clearing temperature. In our studies on the nCB series we have always found $g_{\parallel}$-factor ≈ 3 or even less at the clearing point. In the case of PCH-5 we have calculated $g_{\parallel}$-factors close to 6 near the clearing point.

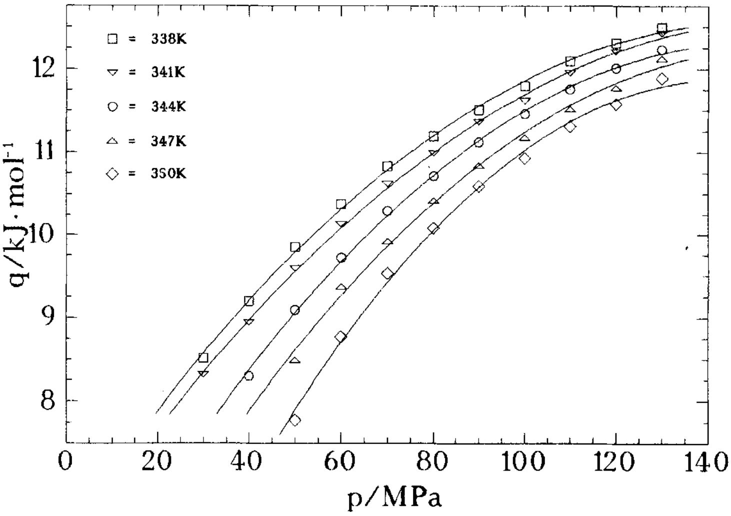

FIG.9 : Nematic potential q as a function of pressure at different temperatures.

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