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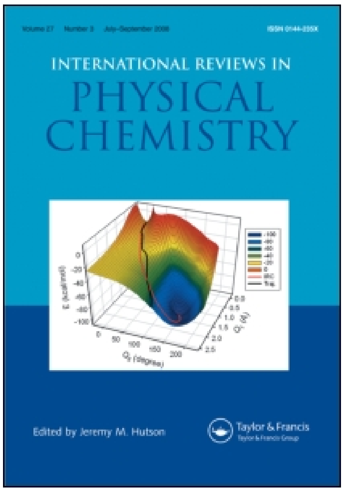

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Dielectric studies under pressure on plastic and liquid crystals

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Dielectric studies under pressure on plastic and liquid crystals

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In the present review we give an account of dielectric studies under high pressure on plastic and liquid crystalline phases. We emphasize the usefulness of employing hydrostatic pressure as an important parameter for varying the average intermolecular distance. Furthermore high-pressure studies are indispensable in order to establish the equation of state and the phase diagram for the substance under investigation, let alone that a wealth of phase transitions is only observed at elevated pressures. In the Introduction we outline the basic concepts of mesophases, dielectric theories and experimental procedures. The essential part of the review deals with the presentation of dielectric results for plastic and liquid crystals under high pressures. Both the static and complex permittivity is treated. The latter yields the dielectric relaxation time whose temperature and pressure dependence enables us to derive the activation enthalpy and activation volume, respectively. The dielectric properties of some cyclic and branched alcohols are compared with previous work on the various ice phases. Recent high-pressure studies on some nematic liquid crystals are presented and discussed. The review also briefly notes other dielectric studies under high pressure in neighbouring fields.

1. Introduction

1.1. *Concept of plastic and liquid crystals*

In general a solid is characterized by a crystal structure, where the centres of mass form a periodic lattice, resulting in a long-range positional order. In the case of anisotropic molecules also a long-range order of the orientations of the molecules will be established. After melting we observe an isotropic liquid that has both translational and orientational freedom. Both kinds of order have been simultaneously destroyed at the melting point.

However, it is well known that various phase transitions may occur associated with a stepwise reduction of these two types of order (Hüller 1980, Schneider 1985, Simon *et al.* 1986), see figure 1. In the case of 'globular' molecules with weakly angle-dependent interactions the molecules may be able to reorient on their lattice sites. Thus the orientational order is lost, but the positional order is still maintained. These orientationally disordered crystals (ODIC) have been formerly characterized as plastic crystals, because many representatives possess a high degree of plasticity (Timmermans 1961). Although less accurate we shall use the term 'plastic crystal' for brevity. This class of substances exhibits large values of entropy and volume changes at the order–disorder phase transition, whereas the changes of the thermodynamic properties at melting are relatively small. According to Timmermans the entropy of melting is less than 2·5 R for plastic crystals. The properties of disordered crystals are described in detail in textbooks (Parsonage *et al.* 1978, Sherwood 1979, Lascombe 1987).

On the other hand orientational order may still be present after melting of strongly anisotropic molecules. For example rod-like molecules have a tendency to form 'nematic' phases in which the long axes of the molecules are roughly oriented parallel to

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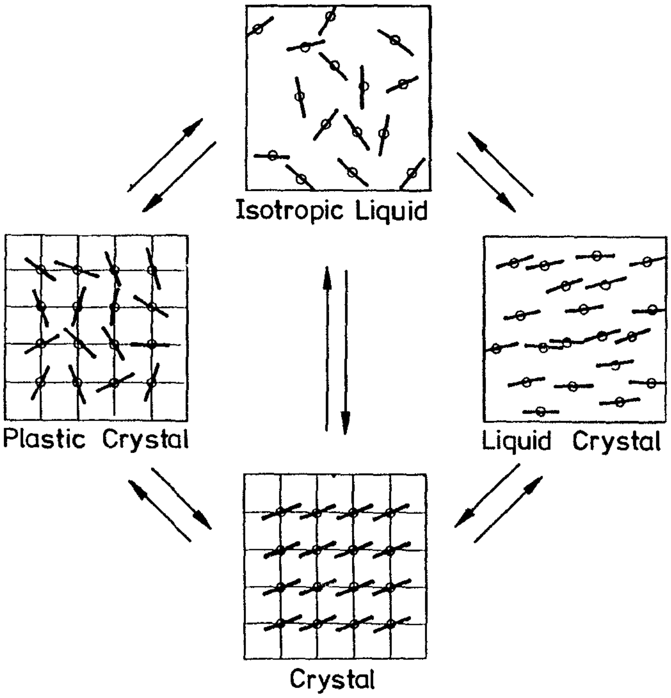


Figure 1. Schematic presentation of possible transitions between the crystal state and the isotropic liquid.

each other. This order will be destroyed on heating at the clearing temperature, yielding an isotropic liquid. In 'smectic' phases the molecules are arranged parallel in layers, but the molecules possess usually considerable translational freedom within the layers. The preferred direction (director) in the nematic-like phases may also change in such a way that a screwed superstructure is imposed, with the helix axis perpendicular to the local director. These phases are termed 'cholesteric'. All these mesophases belong to the group of 'liquid crystals' (LC), whose properties have been reviewed in many articles and textbooks (see e.g. de Gennes 1974, Priestley *et al.* 1975, Luckhurst *et al.* 1979, de Jeu 1980, Vertogen *et al.* 1988, Chiellini 1992). There are also examples of liquid crystals that exhibit not only LC phases, but also uniaxially disordered rotator phases (Nguyen *et al.* 1986, Chledowska *et al.* 1988, Bamezai *et al.* 1990, Janik *et al.* 1992).

It is customary to define an order parameter S for the distribution of the long molecular axes:

$$S=\langle\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2}\rangle, \qquad (1)$$

where $\langle\ \rangle$ means the average over the orientations of all molecules. For isotropic phases S is zero, whereas for perfectly ordered nematic phases S should reach a value of unity. At the clearing temperature S is about 0·3 to 0·4 and increases to about 0·8 at the lowest temperatures. Because of the parallel alignment in the nematic state a reorientation of a molecule perpendicular to the director will be strongly hindered. This angle-dependent part of the intermolecular interactions is called the 'nematic potential'. Maier and Saupe (1959, 1960) have established relations between the order parameter S and the nematic potential q, and other thermodynamic properties. Also in the theory of dielectric relaxation the nematic potential plays an important role that will be treated below.

It is one of the aims of the present review to emphasize the usefulness of investigating the pressure dependence of phase transformations and related properties in condensed systems (for a more general overview see e.g. Samara (1986)). There are a lot of substances, whose phase behaviours change significantly under pressure. New high-pressure induced phases have been found for many plastic crystals, e.g. in cyclohexane (Würflinger 1975, Schulte *et al.* 1987), cyclohexanone (Würflinger *et al.* 1978b), cyclo-octanol (Edelmann *et al.* 1987), neohexanol (Edelmann *et al.* 1991a) and t-butylchloride (Wenzel *et al.* 1982). Phase transitions can be pursued by isobaric temperature variation (using e.g. differential thermal analysis (DTA) or differential scanning calorimetry, (DSC)) and by isothermic pressure changes (e.g. in P, V, T measurements). Valuable structural information is obtained from spectroscopic (Haines *et al.* 1990) and neutron scattering and diffraction studies (Mayer *et al.* 1991, Wilding *et al.* 1991) at elevated pressures.

Some examples of selected phase diagrams are presented in the figures 2 and 3. In the case of cyclohexane deuteration changes significantly the phase situation, leading to two additional solid phases (III and IV). Also for cyclohexanol and 2,2-dinitro-propane deuterated samples have been studied (Bardelmeier *et al.* 1989, Hartmann 1992). However, in the case of 2,2-dinitropropane-d_6 a reduced number of solid phases is observed. In general the coexistence region of plastic phases increases with rising pressure (Karasz *et al.* 1961), but for the rotator phases of some n-alkanes a pressure-limited phase behaviour is observed (Würflinger 1980). Several high-pressure effects occur also in liquid crystalline phases, such as pressure-induced and pressure-limited phases, reentrant and tricritical phenomena (Schneider *et al.* 1986, Shashidhar 1986, 1988, Pollmann *et al.* 1988, Bartelt *et al.* 1989, Raja *et al.* 1989). A broader review was given by Chandrasekhar and Shashidhar (1979).

It should be mentioned that disorder does not only appear in connection with plastic or liquid crystalline phases. Disorder must also be considered for the description of glasses, polymers, ferroelectrics etc. (Descamps 1991). But the present review will concentrate on the formerly mentioned two classes.

1.2. *Dielectic theories*

1.2.1. *Static permittivity*

Polar ODIC phases are characterized by high values for the static permittivity, ε, due to the orientational freedom. Usually the ODIC phases have a cubic structure allowing to treat them as an isotropic system in dielectric studies. Therefore dielectric theories developed for isotropic liquids can also be applied for polar plastic crystals (Hill *et al.* 1969, Böttcher *et al.* 1978). In the case of liquid crystals the anisotropic features of the LC phases must be taken into account. Applying electric or magnetic fields for orienting the sample the permittivity parallel ($\varepsilon_{\parallel}$) or perpendicular ($\varepsilon_{\perp}$) to the director can be measured. Reviews of the dielectric behaviour of liquid crystals have been given by Meier (1975), de Jeu (1978), and Kresse (1983).

The dielectric properties of non-polar compounds are usually described by the Clausius–Mosotti function (CM):

$$\frac{\varepsilon-1}{\varepsilon+2}V_m=\frac{N_A}{3\varepsilon_0}\alpha, \tag{2}$$

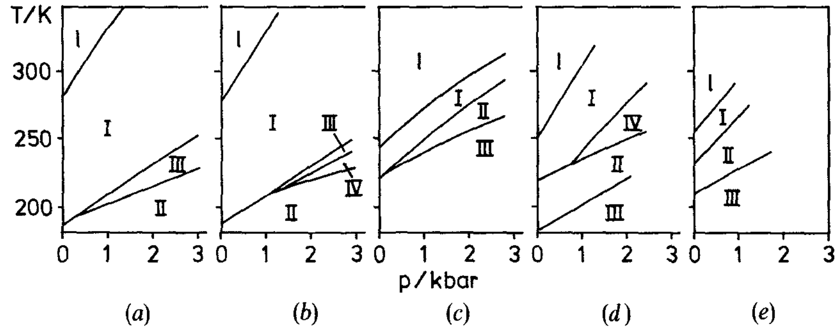


Figure 2. Phase diagrams for (*a*) cyclohexane: C_6H_{12}, (Würflinger 1975), (*b*) C_6D_{12}, (Schulte *et al.* 1987), (*c*) cyclohexanone, (Würflinger *et al.* 1978b), (*d*) t-butylchloride, (Wenzel *et al.* 1982), (*e*) t-butylbromide (Kreul *et al.* 1989).

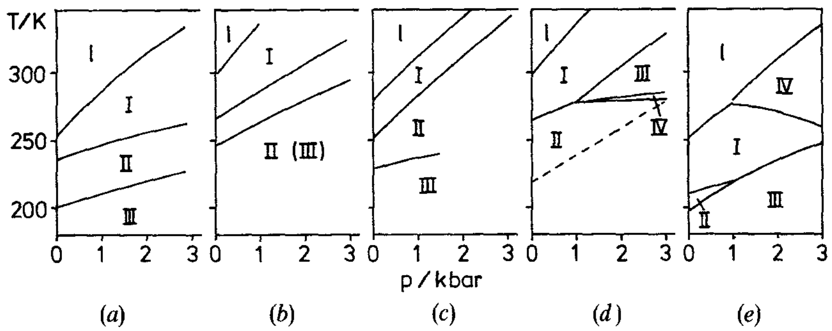


Figure 3. Phase diagrams for (*a*) cylopentanol, (Würflinger *et al.* 1987*b*), (*b*) cyclohexanol, (Pingel *et al.* 1984), (*c*) cyclo-heptanol, (Poser *et al.* 1985), (*d*) cyclo-octanol, (Edelmann *et al.* 1987), (*e*) neohexanol (Edelmann *et al.* 1991). Solid III of the cyclohexanol is a metastable phase that transforms at the lower transition to solid I, whereas solid II transforms at the higher transition line to solid I. The dashed line in the phase diagram of cyclo-octanol corresponds to a phase transition detected in thermal conductivity measurements (Andersson *et al.* 1990).

in which V_m is the molar volume, $\varepsilon_0 = 8{\cdot}854 \times 10^{-12}\,\mathrm{Vs(Am)^{-1}}$, N_A Avogadro's number, and α the molecular polarizability. The CM function changes slightly as a function of pressure and temperature for compressed gases and liquids (Hill *et al.* 1969, Böttcher 1973, Scaife *et al.* 1990, Deul *et al.* 1991). In order to account for the high pressure effects the CM function may be expressed by the dielectric virial equation; see e.g. Cole (1989).

The CM expression has been extended by Debye in adding $\mu^2/3kT$to the molecular polarizability to take into consideration the contribution arising from thermal motions of permanent dipoles μ. This implies that the local field: $E_{loc} = (\varepsilon + 2)E/3$ that has been used to derive the CM equation is also valid in the presence of permanent dipoles. It is well known that the 'Debye equation' fails to describe adequately the dielectric properties of condensed phases. It was left to Onsager (1936) to derive an expression for the local field that better accounts for the interactions between the permanent dipole and its surrounding. The resulting equation is (k = Boltzmann's constant):

$$\mu^2 = \frac{9kT\varepsilon_0 V_m(2\varepsilon + \varepsilon_\infty)(\varepsilon - \varepsilon_\infty)}{N_A \varepsilon(\varepsilon_\infty + 2)^2}. \tag{3}$$

The high frequency permittivity, ε_∞, is usually approximated by $1{\cdot}05\,n^2$ where n is the refractive index (Böttcher 1973).

In fact it has been found that the Onsager equation can approximately describe the dielectric behaviour of many polar liquid and solid rotator phases, except for hydrogen-bonded systems, such as alcohols. In these systems specific correlations are prevailing which might be accounted for by the Kirkwood-g-factor:

$$g=\frac{\left\langle \sum_j \boldsymbol{\mu}_i \boldsymbol{\mu}_j \right\rangle}{\mu^2}=1+z\langle\cos\theta\rangle. \tag{4}$$

In this (simplified) equation z denotes the number of nearest neighbours and θ the angle between them and the central molecule μ_i of a local region. $\langle\ \rangle$ means averaging over all possible configurations, responsible for the local ordering. If neighbouring molecules prefer a parallel ordering ($\theta<\frac{\pi}{2}$) the g factor will exceed unity. For antiparallel arrangements ($\theta>\frac{\pi}{2}$) g is below unity. Typical dipole correlations for polar compounds, including liquid crystals are described in the literature (Böttcher *et al.* 1973, 1978, de Jeu 1980).

In general it is difficult to calculate g by means of equation (4) in a straightforward manner, because the local structure is not always known. There are only few examples in literature where the Kirkwood-g factor has been evaluated with the aid of a rigorous statistical-mechanical treatment, e.g. for ice (Nagle 1974) and succinonitrile (Descamps *et al.* 1977). Therefore one very often uses an equation derived by Fröhlich that corresponds formally to the Onsager equation in replacing μ^2 by $g\mu^2$, that is, the g factor is calculated from the deviation of the Onsager dipole moment from the 'true' dipole moment μ_{gas}, derived from measurements in the gas phase. However, the simplifications and limitations of this procedure must be borne in mind (Hill *et al.* 1969, Franck *et al.* 1978). Especially the choice of ε_∞ is be no means simple. Nevertheless the Kirkwood-g-factor is of fundamental importance being a measure of orientational order in condensed systems (Steinhauser 1983). If there is complete orientational order on a long-range scale then g either vanishes or diverges (resulting in ferroelectricity) depending on whether the net dipole moment of the crystallographic cell is zero or not.

Strong deviations of the Onsager dipole moment from μ_{gas} are also observed for molecules whose shape differs considerably from a sphere. A certain improvement is obtained when the spherical cavity of the Onsager model is replaced by an ellipsoidal cavity (Böttcher 1973), but there is too much arbitrariness for the correct choice of the axes of the ellipsoid. Furthermore the anisotropy of the polarizability should also be taken into account. A comprehensive review concerning the statistical-mechanical theory of dielectric polarization has been given by Schröer (1985).

It is indispensable to account for the anisotropy of the polarizability in the treatment of liquid crystals. Maier and Meier (1961) extended the Onsager theory to nematic liquid crystals. They considered two principal values α_l and α_t for the polarizability of an elongated molecule whose dipole moment μ has the angle β with the long axis (= direction of α_l): That is $\mu_l=\mu\cos\beta$ and $\mu_t=\mu\sin\beta$. For the calculation of the cavity factor $h=3\varepsilon/(2\varepsilon+1)$ and the reaction field factor $f=(\varepsilon-1)\,[2\pi\varepsilon_0 a^3(2\varepsilon+1)]^{-1}$ the anisotropy of the permittivity is not taken into account (a = radius of the spherical cavity). In the expression $F=(1-f\alpha)^{-1}$ the anisotropy of the polarizability is ignored. The resulting equations are, where N denotes the number of molecules per unit volume (for a detailed discussion see e.g. de Jeu (1980) or Vertogen *et al.* (1988)):

$$\langle\alpha\rangle_{\parallel}=\tfrac{1}{3}[\alpha_l(2S+1)+\alpha_t(2-2S)], \tag{5}$$

$$\langle\alpha\rangle_\perp = \tfrac{1}{3}[\alpha_l(1-S)+\alpha_t(2+S)], \tag{6}$$

$$\langle\mu_\parallel^2\rangle = \tfrac{1}{3}[\mu_l^2(2S+1)+\mu_t^2(1-S)] = \tfrac{1}{3}\mu^2[1-(1-3\cos^2\beta)S], \tag{7}$$

$$\langle\mu_\perp^2\rangle = \tfrac{1}{3}[\mu_l^2(1-S)+\tfrac{1}{2}\mu_t^2(2+S)] = \tfrac{1}{3}\mu^2[1+\tfrac{1}{2}(1-3\cos^2\beta)S], \tag{8}$$

$$\varepsilon_\parallel = 1+(NhF/\varepsilon_0)(\langle\alpha\rangle_\parallel + F\langle\mu_\parallel^2\rangle/kT), \tag{9}$$

$$\varepsilon_\perp = 1+(NhF/\varepsilon_0)(\langle\alpha\rangle_\perp + F\langle\mu_\perp^2\rangle/kT). \tag{10}$$

These equations allow us to draw some general conclusions for the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$. If $3\cos^2\beta = 1$ ($\beta \approx 55°$) then $\Delta\varepsilon$ is solely determined by the anisotropy of the polarizability. For $\beta < 55°$ the permanent dipole contributions enlarge $\Delta\varepsilon$. For $\beta > 55°$ the dipole contribution counteracts the positive anisotropy of the polarizability. The temperature dependence of the orientational polarization is proportional to S/T, whereas that of the induced polarization is like S. From this the temperature dependence of $\Delta\varepsilon$ can be qualitatively predicted in accordance with experimental observations (de Jeu 1980). If the parallel component of μ is predominant ($\mu_l \gg \mu_t$) and significantly exceeding the contribution from α, it follows from equations (7) and (9) that $\varepsilon_\parallel - 1$ is approximately proportional to $(2S+1)/T$ (Urban 1992).

1.2.2. *Complex permittivity*

Studies of the dielectric dispersion give valuable information on the dynamics of molecular reorientation. For sufficiently high frequencies the reorienting molecules lag behind the field that results in a decrease of the permittivity and the appearance of the 'dielectric loss'. It is convenient to express the dielectric constant as a 'complex permittivity'

$$\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon''. \tag{11}$$

The real and imaginary parts are derived from capacitance and conductivity measurements, respectively (Hill *et al.* 1969).

Assuming an exponential decay function for the dielectric relaxation and a single relaxation time τ, leads to the well-known Debye equations, where $\omega = 2\pi f$ (f = frequency of the applied field), and $\varepsilon = \varepsilon(\omega = 0)$ = static permittivity:

$$\varepsilon' - \varepsilon_\infty = \frac{\varepsilon - \varepsilon_\infty}{1+\omega^2\tau^2}, \tag{12}$$

$$\varepsilon'' = \frac{\varepsilon - \varepsilon_\infty}{1+\omega^2\tau^2}\,\omega\tau. \tag{13}$$

A plot of ε'' against ε' results in a semicircle, known as Cole–Cole plot. The maximum of the loss curve is related to the inverse relaxation time: $\omega_{\max} = 1/\tau$. Strictly speaking one should distinguish between the macroscopic (τ) and microscopic (τ') relaxation time (Brot 1975). Several relations have been proposed in literature, one of which is (Hansen and McDonald 1986):

$$\tau = \left(\frac{3\varepsilon g}{2\varepsilon + 1}\right)\tau'. \tag{14}$$

According to this equation τ and τ' are not significantly different. Consequently we shall use the macroscopic relaxation time throughout this paper.

In practice more or less deviations from the ideal 'Debye behaviour' are observed. The semicircles appear flattened and/or skewed. Several empirical extensions of the Debye equation have been suggested to describe the experimental findings. We mention here the equation of Havriliak–Negami (HN), Jonscher, and the Dissado Hill function (DH) which all contain the Debye equation as a special case (for details see e.g. Hill *et al.* (1969), Böttcher *et al.* (1978), Jonscher (1983), Dissado *et al.* (1985)). Representing the complex permittivity in form of the spectral shape function $G^*(\omega)=[\varepsilon^*(\omega)-\varepsilon_\infty]/[\varepsilon(0)-\varepsilon_\infty]$, the HN and DH equations read as follows:

$$\text{HN:}\quad G^*(\omega)=[1+(\mathrm{i}\omega\tau_0)^{1-\alpha}]^{-\beta}, \tag{15}$$

with Cole–Cole (CC): $\beta=1$, Cole–Davidson (CD): $\alpha=0$, as special cases,

$$\text{DH:}\quad G^*(\omega)=(1+\mathrm{i}x)^{n-1}{}_2F_1[1-n,1-m;2-n;(1+\mathrm{i}x)^{-1}]/F(0), \tag{16}$$

in which ${}_2F_1[,;;]$ is the Gaussian hypergeometric function, $F(0)={}_2F_1(1-n,1-m;2-n;1)$, and $x=\omega/\omega_p$, ω_p being of the order of $\omega_{\max}$.

According to classical treatments deviation from an ideal Debye behaviour is explained as a superposition of uncorrelated relaxations, corresponding to a distribution of relaxation times about a principal value τ_0. Neither $1/\tau_0$ nor ω_p correspond exactly to $\omega_{\max}$, but we define $\tau=1/(\omega_{\max})$ also for the non-Debye-like curves. The exponents α and β as well as m and $1-n$ are generally used as adjustable parameters to fit experimental data to the loss functions. The Jonscher equation

$$\varepsilon''=\frac{A}{(\omega/\omega_p)^{-m}+(\omega/\omega_p)^{1-n}} \tag{17}$$

is related to the DH function in that m and $n-1$ describe in both cases the slopes of $\log(\varepsilon'')$ against $\log(\varepsilon')$ in the low and high frequency limit. In the DH theory the parameters m and n are claimed to have physical significance, describing the order and correlations within clustered regions. Apart from the theoretical background the Jonscher equation seems to be very convenient from a purely practical point of view. We recently compared the various loss functions in the context of the dielectric behaviour of some plastic alcohols (Würflinger 1991).

Dielectric relaxations are rate processes and correspondingly theories of Arrhenius and Eyring can be applied (Whalley 1966, Hill *et al.* 1969). We obtain so-called activation parameters from the temperature and pressure dependence of τ, using the subscripts A for Arrhenius and E for Eyring, respectively.

$$\Delta H^{\#}_{\mathrm{A}}=R\left(\frac{\partial\ln\tau}{\partial 1/T}\right)_p, \tag{18}$$

$$\Delta H^{\#}_{\mathrm{E}}=R\left(\frac{\partial\ln(T\tau)}{\partial 1/T}\right)_p=\Delta H^{\#}_{\mathrm{A}}-RT, \tag{19}$$

$$\Delta U^{\#}=R\left(\frac{\partial\ln\tau}{\partial 1/T}\right)_V=\Delta H^{\#}_{\mathrm{A}}-(\partial p/\partial T)_V T\Delta V^{\#}, \tag{20}$$

$$\Delta V^{\#}=RT\left(\frac{\partial\ln\tau}{\partial p}\right)_T. \tag{21}$$

The activation volume $\Delta V^{\#}$ is a measure for the extra space needed to reach the transition state. In the framework of the present paper the relaxation process is usually considered as a reorientation of a molecule interacting with its neighbours. Therefore

$\Delta V^{\#}$ is understood as the extra volume the surrounding must provide to enable a rotation of the species. It is the most interesting quantity that can be derived from high pressure kinetic studies.

Assuming the transmission coefficient of the Eyring equation to be unity also permits evaluation of the activation entropy (Johari and Dannhauser 1969). Many authors prefer the activation energy instead of the activation enthalpy, because the variation of τ at constant volume yields an energy barrier not affected by density changes and hence by changes of the intermolecular distance. It is one of the advantages of high-pressure researches that these quantities can be distinguished and determined, provided P, V, T data are available. It should be mentioned that usually reported activation energies derived from ambient pressure experiments are in fact activation enthalpies. But we shall use the term activation energy only for the temperature dependence of τ under isochoric conditions.

There are a lot of relations between the activation parameters which have been fully discussed by Whalley (1966). One interesting equation relates the pressure dependence of the activation enthalpy to the temperature dependence of the activation volume:

$$\left(\frac{\partial \Delta H_{\mathrm{E}}^{\#}}{\partial p}\right)_T = \left(\frac{\partial \Delta V^{\#}/T}{\partial 1/T}\right)_p. \tag{22}$$

This equation follows easily from the rule of Schwarz employed on the function $\ln \tau$, and can be used to test the consistency of experimental results. Another interesting relation is found for the slope $(\mathrm{d}p/\mathrm{d}T)_\tau$ at constant relaxation time:

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_\tau = \frac{\Delta H^{\#}}{T\Delta V^{\#}}. \tag{23}$$

In the case of nematic liquid crystals the dielectric relaxations must be distinguished for measurements parallel and perpendicular to the director. For the field along the director reorientations of μ_1 can contribute to $\varepsilon_{\parallel}$ through a rotation about a short molecular axis. In this case the rotation is strongly opposed by the neighbouring molecules. Rotations around the long molecular axis are obviously easily accomplished and not affected by the nematic potential. This rotation leaves μ_t unchanged and hence the main contribution to $\varepsilon_{\perp}$ comes from μ_t. Because of the different interactions involved in these relaxation processes $\tau_{\perp}$ is much shorter than $\tau_{\parallel}$. We will come back to this point below when discussing the dielectric relaxation for 4,4′-pentylcyanobiphenyl.

Meier and Saupe (1966) and Martin *et al.* (1971) have worked out a theory in which so-called retardation factors $g_{\parallel}$ and $g_{\perp}$ (not to be confused with Kirkwood g factors) are defined as ratios of the relaxation time in the nematic phase and that of a hypothetical state with $q=0$. If $\mu_t=0$, then $\tau_0=\tau(q=0)$ can be obtained from an extrapolation of τ_{is}, that is, from dielectric relaxation measurements in the isotropic phase (de Jeu 1980, Kresse 1983). In this respect some alkylcyanobiphenyls with $\mu_t=0$ are of particular interest. The following equation was derived that connects the nematic potential q with the retardation factor:

$$g_{\parallel}=\tau_{\parallel}/\tau_0=(kT/q)\left[\exp(q/kT)-1\right]. \tag{24}$$

q/kT is a monotonously increasing function of the order parameter S. Davies *et al.* (1976) have satisfactorily tested the Martin–Meier–Saupe theory through measurements on 4,4′-n-heptylcyanobiphenyl. Recent high pressure measurements on the pentyl-homologue (5CB) will be presented below. It should be mentioned that a profound discussion must also take into consideration the influence of the viscosity on the dielectric relaxation time (Böttcher *et al.* 1978, de Jeu 1980).

2. Experimental methods

Earlier reviews on dielectric measurements under pressure have been given by Whalley (1966), Hill *et al.* (1969), and Scaife (1971). Dielectric studies are also partially considered in some conferences on high pressure science and technology, e.g. Vodar *et al.* (1980), Schilling *et al.* (1981), Backmann *et al.* (1982), Homan *et al.* (1984), Trappeniers *et al.* (1986), and Holzapfel *et al.* (1990). The main problems arising in high pressure dielectric measurements are:

(*a*) Change of the geometric capacitance with pressure.
(*b*) Occurrence of pressure gradients.
(*c*) Feedthroughs for the electrical leads.
(*d*) Separation of the pressure medium from the substance.
(*e*) Reactions of the substance under study with the material of the dielectric cell.

Depending on the experimental conditions different devices have been established. We briefly recall some examples of dielectric studies of fluids, because their features might also be relevant for investigations of solids.

2.1. *Studies of fluid phases*

Many high pressure devices are reported for the investigation of liquid or fluid phases. Three-terminal electrodes sets are described for the study of molecular liquids from lower to room temperatures up to pressures of about 500 MPa (Mopsik 1967, Johari *et al.* 1968, Brazier *et al.* 1969, Srinivasan *et al.* 1974, Vij *et al.* 1978, Scaife *et al.* 1985). Very often the dielectric cell is combined with a bellows dilatometer for a simultaneous measurement of permittivity and density. The bellows serves also to separate the substance under investigation from the pressure medium. Otherwise pistons with O rings or other sealings are used.

Franck and coworkers developed a series of dielectric cells for measurements at high temperatures and pressures up to the critical region of many organic and inorganic compounds (Franck *et al.* 1978a, b, Harder *et al.* 1989, Uematsu *et al.* 1989, Hill *et al.* 1990). Large difficulties were encountered in these experiments due to the corrosive properties of the substances under these extreme conditions.

For dielectic studies at higher pressures piston cyclinder apparatus are employed. Johari *et al.* (1972) describe a dielectric cell to be used to 2·5 GPa. Pressure is applied to the piston by means of a hydraulic press. Due to friction between the cylinder and piston a relatively large hysteresis in the pressure reading occurs that limits the accuracy of the pressure measurement. Forsman *et al.* (1986) report on a dielectric cell for measurements up to 1 GPa. A manganin coil was used for pressure calibration. Both devices have been employed for dielectric studies of liquid and glassy systems.

The dielectric cells so far mentioned were essentially used for measurements at comparatively low frequencies (<10 Mhz). With increasing frequencies errors caused by lead impedances may affect the accuracy of the measurements seriously that requires careful corrections (Atanov *et al.* 1969, Scaife *et al.* 1976, Würflinger 1978a, Kreul 1991). Considerable experimental problems are encountered in studies at microwave frequencies. Pottel *et al.* (1979) describe an apparatus for electromagnetic cm-wave reflection measurements at 17·6 GHz at room temperature and pressures up to

100 MPa. A self-sealing dielectric window of high-density ceramic Al_2O_3 served to separate the pressurized substance from the wave-guide.

2.2. *Studies of solid phases*

The permittivity of brittle solids or crystals can be studied with a parallel-plate capacitor the electrodes of which are spring-loaded to ensure good contact to the sample. The surfaces of the crystals must be well prepared and polished. Using different specimens appropriately cut from oriented single crystals permits one to determine the dielectric tensor (see e.g. Munn *et al.* (1973)). The pressure is transmitted by a compressed liquid or directly through the upper moving-electrode. Thus the cell constant changes under pressure and its calibration is complicated. The fixed-electrode method corresponds to the procedures described for liquids. Therefore the sample will be compressed hydrostatically and deformed. This method is especially suitable for ODIC phases because of their plasticity. Both methods have been employed by Whalley and coworkers to study the various forms of the high-pressure ice phases (Whalley 1966, Whalley *et al.* 1973). The authors applied also the anvil method to reach very high pressures. Johari *et al.* (1975) studied very slow relaxation phenomena in ice Ih by means of thermally stimulated depolarization measurements. A large pressure range was also covered by a series of investigations on mainly inorganic systems by Samara (1966, 1968, 1976). The temperature and pressure dependences of the dielectric constants of semiconductors have been studied as well (Samara 1983).

Many further examples can be given for solid state physics applications. The dielectric constants and their pressure and temperature derivatives for ionic crystals have been recently reviewed by Shanker snd Dixit (1991). We recall some literature work that is rather illustrative than comprehensive. Preu *et al.* (1984) investigated the dielectric constants of alums up to 700 MPa. Single crystals were cut into disks and measured between spring-loaded brass electrodes. Similar measurements have been performed by Smith *et al.* (1974) on KBr, depositing aluminium electrodes directly on the crystal surfaces. Peercy *et al.* (1975) measured the static dielectric constant on disks of fused SnJ_4 in a piston cylinder apparatus up to a 36 GPa. Bertie *et al.* (1977) used a coaxial dielectric cell up to 150 MPa that was similar to one applied by Whalley *et al.* (1968). The pressure is transmitted by pistons on a parallel-plate cell. Belokopytov *et al.* (1985) describe an apparatus for the study of the super-high frequency dielectric properties of ferroelectrics at low temperatures under uniaxial compression. Measurements were made for $KTaO_3$. Hikita *et al.* (1990) performed electric measurements down to 4·2 K using a precise pressure–temperature control system.

We notice some other examples of high pressure studies on ODIC or molecular crystals: Chew *et al.* (1973) describe an assembly for simultaneous measurements of permittivity and volume changes up to 500 atm. The pressure is transmitted by a tension spring through a piston on the sample. Costantino *et al.* (1973) developed a capacitor for dielectric measurements in liquids and solids in the temperature range 10 to 300 K and up to 1·1 GPa. Sample and pressurized medium were identical, so problems arising from the possible contamination caused by the pressurized gas (usually helium, argon or nitrogen) are avoided. On the other hand the precise pressure determination renders rather difficult after solidification of the substance. Several polar plastic crystals have been studied by the author and coworkers using cylindrical capacitors with fixed electrodes (Würflinger (1981, 1991) and references therein).

Bui Ai *et al.* (1979) describe a high pressure apparatus for dielectric measurements up to 15 MHz and 150 MPa. They studied the dielectric loss of polyethylene and insulating materials used for submarine telecommunication cables. The authors also review briefly dielectric measurement methods in polymers under high pressure (Giam *et al.* 1982). A high pressure apparatus for the dielectric investigations of polymers was established by Heinrich and Stoll (1985a). They re-examined the glass relaxation in polyvinylacetate and polyvinylchloride up to 500 MPa. Hampton *et al.* (1989) report on dielectric measurements of vitreous materials under pressure up to 7 GPa. Details of the experimental equipment, the data acquisition as well as the necessary corrections are presented.

2.3. *Studies of liquid crystals*

Yasuda *et al.* (1984a) investigated solid MBBA up to 600 MPa using a parallel plate capacitor cell with strips of the transparent tin oxide conducting coating. The sample was sandwiched between the electrodes the distance of which was fixed to 0·3 mm with the aid of Teflon spacers. The same set-up was used to study ferroelectric smectic liquid crystals. The sample was introduced into the cell in the isotropic phase, subjected to a low a.c. field and then slowly cooled down to the smectic-C phase for the alignment (Yasuda *et al.* 1985).

Poser (1987) and Kreul (1991) employed a previously described high pressure cell (Würflinger 1978a, 1981) and designed new capacitors made of cylindrical electrodes for the study of liquid and plastic phases. It was shown recently that these dielectric cells can also be used for the measurements of slow relaxation processes occurring in some nematic liquid crystals (Kreul 1991, Kreul *et al.* 1992, Urban *et al.* 1992).

3. Results of dielectric studies under pressure

3.1. *Plastic crystals*

3.1.1. *Non-polar compounds*

Only a few studies are concerned with non-polar substances. Chew and Chan (1973) determined the permittivity and volume changes of cyclohexane and neopentane up to 50 MPa. Part of the results are shown in figure 4 together with our own measurements (Würflinger 1981). After freezing cyclohexane forms a plastic phase solid I that transforms below −87°C to a relatively hard and brittle phase solid II. At low pressures Chew and Chan observed a decrease of ε on passing the solid I–II transition, whereas above 25 MPa ε increased. Obviously voids had been produced in the sample at the lower phase transition that results in too small values for the dielectric constant. Application of pressure destroys the holes, and the permittivity increases as expected from the increase of density. The increase in ε according to our measurements is less pronounced, because our cylindrical capacitor causes larger pressure gradients in non-plastic solid phases. In fact, many published data of normal pressure permittivities are questionable, because holes and cracks appeared after solidification. This has also been observed for polar compounds, e.g. for phenol (Bertie *et al.* 1977) and t-butylbromide (Kreul *et al.* 1989). Our measurements at 1000 bar reveal a very small step due to the onset of an additional pressure induced phase transition (Würflinger 1975).

Constantino *et al.* (1975) investigated solid methane at low temperatures for which three solid phases are known to exist. The authors suggest the possible existence of a fourth phase at higher pressures due to a dielectric anomaly. Within experimental error the CM function is constant across the melting transition and is independent of density in the solid phase. The data are discussed in terms of a model based on octupole-induced dipoles.

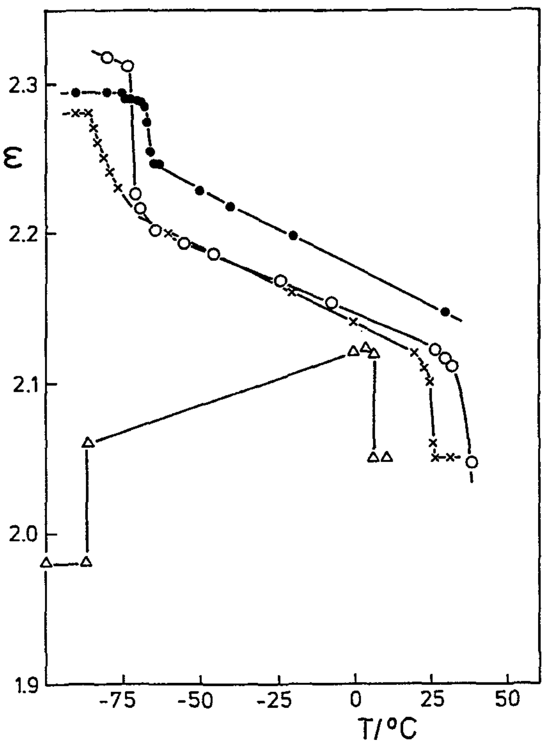


Figure 4. Permittivity of cyclohexane for different pressures: 1 atm (△), Crowe *et al.* 1951; 500 atm (○), Crew *et al.* 1973, 400 bar (×) and 1000 bar (●) Würflinger 1981.

Scaife and coworkers (1985) who performed a lot of measurements on liquid alkanes included also the freezing region in their investigations. They fitted the density dependence of CM to an empirical expression:

$$\frac{\varepsilon-1}{\varepsilon+2}V_m = a_0 + a_1\rho + a_2\rho^2 + a_3\rho/T, \tag{25}$$

and arrived at a similar conclusion as Constantino *et al.* concerning the constancy of CM on freezing. Deleting the temperature term equation (25) can be used both for the liquid and the solid state. Thus variations of density can be predicted by measuring the permittivity in the solid state, and hence enthalpy changes using the equation of Clausius–Clapeyron.

3.1.2. *Non-hydrogen-bonded polar compounds*

Cyclohexanone is a typical representative of the plastic crystals showing an order–disorder transition at 220·3 K and a melting temperature at 242·4 K (Würflinger *et al.* 1978b). This solid state transformation splits with increasing pressure yielding a second ODIC phase, see figure 2. The pressure dependence of the permittivity at 273 K is shown in figure 5. ε increases on freezing, and decreases somewhat at the intermediate solid–solid transition showing that some part of the orientational freedom must be frozen in (Würflinger 1980). Finally the permittivity decreases sharply at the solid II–solid III transition to values customary for ordered molecular crystals (not shown on the figure). The Onsager dipole moment of liquid and ODIC phases is very close to the gas dipole moment, in other words: the Kirkwood g factor is very close to unity. A

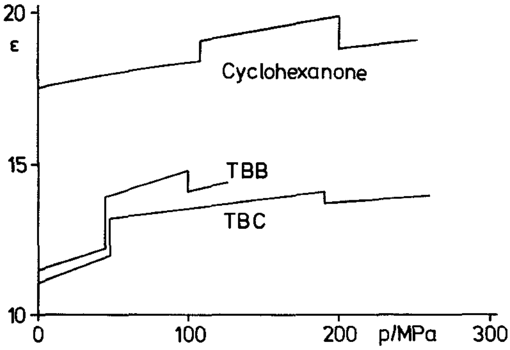


Figure 5. Permittivity of cyclohexanone (Würflinger 1980), t-butyl-chloride (Wilmers *et al.* 1984), and t-butylbromide (Kreul *et al.* 1989) at 273 K as a function of pressure. First step: increase in ε on freezing, second step: decrease in ε at an intermediate transition between two ODIC phases.

small temperature dependence of g is observed within the ODIC phases but the change in g along a phase transition line is almost negligible. The g factor changes practically continuously in the freezing region (apart from a very small step). So the Onsager equation plays a similar role for some polar plastic crystals as the Clausius–Mosotti function for the non-polar compounds mentioned above.

Also the t-butyl compounds very often represent molecules with globular shape which have been comprehensively reviewed by Urban (1981). It might be interesting to compare the thermodynamic and dielectric properties of t-butylchloride (TBC) with t-butylbromide (TBB). Both substances exhibit two ODIC phases, see figure 2, but for TBC the second ODIC phase appears only at high pressures (Wenzel *et al.* 1982, Wilmers *et al.* 1984). Both TBC and TBB (Kreul *et al.* 1989) show an increase in ε on freezing and a decrease at the intermediate solid–solid transition, similar to cyclohexanone (see figure 5). In the case of TBC the Kirkwood g factor is somewhat larger than for TBB, but deviates not too much from unity as to indicate specific correlations.

Usually, large changes in entropy and volume are observed at the order–disorder transition, accompanied by corresponding large changes in the permittivity, see table 1. In the case of intermediate transitions between different ODIC phases both the thermodynamic and permittivity changes are small. However, there are exceptions from this statement, e.g. in neohexanol that will be discussed below. Transitions between the different phases can preferably be achieved by isobaric temperature variations, because the slopes $\mathrm{d}T/\mathrm{d}p$ of the phase boundaries are relatively flat.

Using available P, V, T data one may also compare the derivatives $(\partial \log g/\partial \log \rho)_T$ and $(\partial \log g/\partial \log T)_\rho$. It was found that for the non-hydrogen-bonded substances studied the g factor is not very temperature-dependent under isochoric conditions but changes significantly as a function of density at constant temperature. This reflects the sensibility of the local structure against a variation in the average intermolecular distance. The density dependence of the Kirkwood g factor has also been discussed in the frame of an extended model derived from Vedam's (1983) linear elasto-optic relationships (Diguet 1986).

For the plastic crystals just mentioned dielectric absorption measurements have only been carried out at normal pressure, e.g. for cyclohexanone (Corfield and Davies 1964) and the t-butyl compounds (Urban 1981). The dielectric relaxation time is of the order of 10^{-11} s at the melting temperature without significant changes on freezing. Its

Table 1. Thermodynamic and dielectric properties of some plastic crystals.

Transition	T K	P MPa	ΔS J(mol K)$^{-1}$	ΔV cm^3(mol)$^{-1}$	$\varepsilon(0)$ below/above the phase tr.
Cyclohexanone	(Würflinger 1980, 1981)				
melting	272·7	100	4·74	1·29	19·3/18·5
solid II/I	246·5	100	1·76	0·46	20·1/21·4
solid III/II	238·7	100	33·3	5·82	3/20·7
t-Butylchloride	(Wilmers *et al.* 1984)				
melting	302·6	100	6·28	3·4	12·3/11·2
solid II/I	276	200	3·8	1·45	13·5/13·9
solid II/IV	248·6	200	16·1	2·2	5/15
t-Butylbromide	(Kreul *et al.* 1989)				
melting	255·5	0·1	7·7	3·93	13/12
solid II/I	233	0·1	4·5	1·8	14·7/15·4
solid III/II	208	0·1	27·2	5·43	3·5/16·5
Neohexanol	(Edelmann *et al.* 1991a, b)				
melting (SI)	250·6	0·1	6·8	2·10	20·2/20
melting (SIV)	290	132·7	4·4	1·40	14·5/14·5
solid II/I	210·4	0·1	6·2	0·50	3/25·2
solid III/II	198·6	0·1	22·7	5·20	2·5/2·8
solid I/IV	273·2	156	3·5	−0·20	19·5/18·2
Neopentanol	(Waldinger 1990, Kreul 1991)				
melting	331·4	0·1	12·25	8·0	10/10
solid II/I	236·2	0·1	18·9	4·0	3/25

temperature dependence yields activation enthalpies of $\Delta H_E^{\#} = 9{\cdot}4$ and 7 kJ mol^{-1} for liquid and solid cyclohexanone, respectively. In the case of TBC and TBB the values are: 2·85 and 3·5 for the liquid and 3·4 and 4·2 kJ (mol)$^{-1}$ for the solid state. These results reflect the ease of molecular rotation that is only little affected after solidification.

3.1.3. *Hydrogen-bonded polar compounds*

It is well known that various high pressure ice phases exhibit ODIC character that has been reviewed elsewhere (Whalley 1966, 1976, Franks 1972, Whalley *et al.* 1973, Engelhardt 1976, Ross 1985). Only some essential features are repeated here. A sketch of the phase diagram is shown in figure 6. All phases adjacent to the melting curve (ice I, III, V, VI, VII) are characterized by high values for the static permittivity and slow relaxation phenomena. In ice II, VIII and IX the molecular orientations are ordered. Order–disorder transitions are observed between ice III and IX, and ice VII and VIII, respectively. The phase boundaries between different ODIC phases are essentially vertical lines. Therefore transitions between them can be achieved by decompressing at constant temperature (Wilson *et al.* 1965). Figure 7 presents the permittivity and the relaxation time as a function of pressure, showing the increase in ε at each phase transition. A very strong increase in ε and hence in the g factor with decreasing temperature is observed for Ice VI, indicating a ferroelectric ordering that can be described with the Curie–Weiss law. Ice VII consists of two interpenetrating cubic Ic sub-lattices. After transformation to ice VIII the two sublattices are completely antiparallel, resulting in $g \approx 0$ for the Kirkwood g factor.

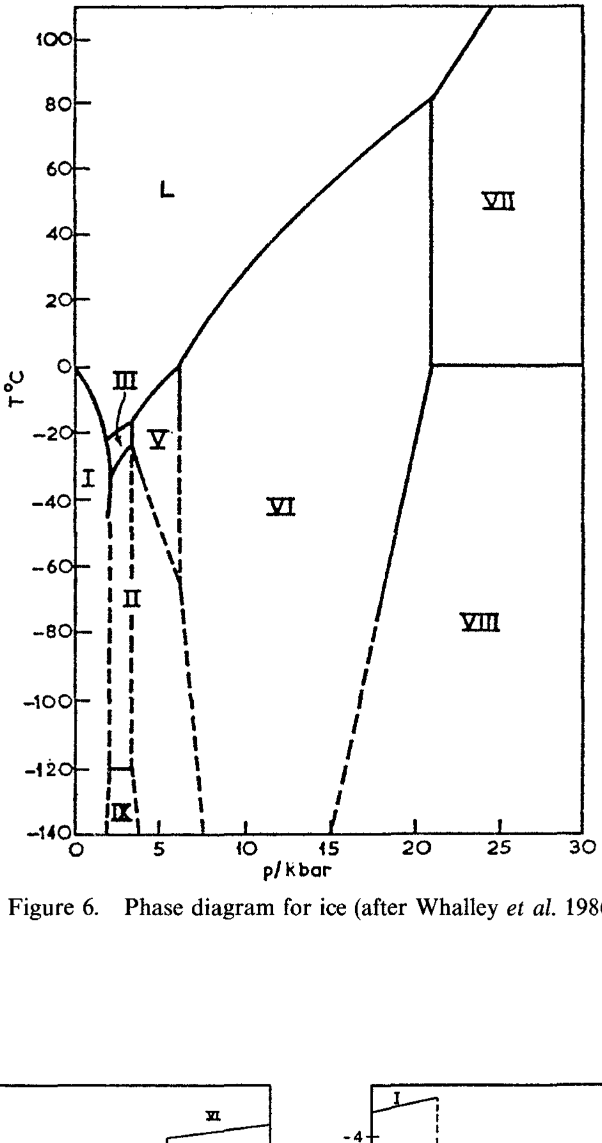
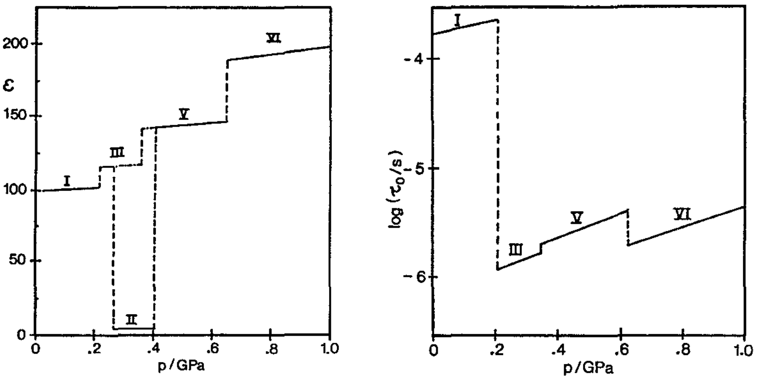


Figure 6. Phase diagram for ice (after Whalley *et al.* 1986).



(*a*) (*b*)

Figure 7. (*a*) Permittivity at −30°C and (*b*) dielectric relaxation time at −23·4°C for various ice phases as a function of pressure (after Wilson *et al.* (1965)).

The dielectric relaxation is Debye-like in ice Ih and Ic, but a certain distribution of relaxation times is observed for the disordered ice phases III, V, and VI. The relaxation time for the solid ice phases is about 10^6 larger than in water, showing that different mechanisms are responsible for the relaxation in the liquid and solid state. Activation parameters derived from the dielectric relaxation yield approximate values for $\Delta H_E^{\#} = 50\,\mathrm{kJ\,(mol)^{-1}}$ and $\Delta V^{\#} = 4{\cdot}5\,\mathrm{cm^3\,(mol)^{-1}}$, but ice I exhibits a significantly lower value, see table 2. The activation enthalpy is equivalent to the energy of three H bonds. The positive activation volume can be explained through the formation of D and L defects.

A series of cyclic and branched alcohols have been investigated in the past and reviewed recently (Würflinger 1991). We mention also recent calorimetric (Mayer *et al.* 1990) and extensive spectroscopic studies at normal pressure (Sciesinska 1991) as well as high-pressure thermal conductivity investigations (Andersson *et al.* 1989, 1990). Pressure-induced ODIC phases have been found (Edelmann *et al.* 1987, 1991a), that is, two for cyclo-octanol and one for 2,2-dimethyl-butan-1-ol (neohexanol) which are not observed at atmospheric pressure, see figure 3. Neohexanol is particularly interesting,

Table 2. Static permittivity and activation parameters for some hydrogen-bonded ODIC phases.

	T	p		$\Delta H^{\#}$	$\Delta V^{\#}$	τ
Phase	K	MPa	ε(0)	$\mathrm{kJ\,(mol)^{-1}}$	$\mathrm{cm^3\,(mol^{-1})}$	10^{-8} s
Ice (Whalley 1966, Franks 1972, Chan *et al.* 1965)						
SI	249·8	0·1	97·5	55·6	2·9	16800
SIII	243	300	117	48·5	4·5	275
SV	243	500	144	48·1	4·8	720
SVI	243	800	193	46	4·4	600
SVII	295	2200	108	48·5	2·5	23
Cyclopentanol (Würflinger 1982)						
SI	243	0·1	28·6	40	5·2	1·1
SII	243	100	33	43·2	5·0	1·9
Neopentanol (Kreul 1991)						
SI	273	0·1	19·6	49	1·8	1·8
Cyclohexanol (Pingel *et al.* 1984)						
SI	283	0·1	17·6	43	5	1·8
SI	263	0·1	19·0		8·6	5·6
Neohexanol (Edelmann *et al.* 1991b)						
liq	273	0·1	14·48	51·1		1·4
SI	273	100	18·85	55·4	5	5·6
SIV	273	200	18·58	63·7	11	6·5
Cycloheptanol (Poser *et al.* 1985, 1987)						
SI	273	0·1	19·3	35·6	10·4	3·9
SII	273	100	21·3	48·1	4·8	9·9
Cyclooctanol (Poser *et al.* 1987, 1988)						
SI	280	100	17·56	64·3	16·1	10·6
SIII	280	125	18·44	58	11·5	18
SIV	280	150	22·01		11·9	43

because the phase boundary between the plastic phases I and IV intersects the melting curve, resulting in a solid/solid/liquid triple point. Such triple points are typical for the ice phases, see figure 6.

The ODIC phases of cyclohexanol and neopentanol are of cubic structure, whereas those of cyclopentanol are hexagonal. Correspondingly the latter substance exhibits anisotropic effects, resulting in varying values for the permittivity, depending on the direction of growth of the crystals (Green *et al.* 1972). None of the other plastic phases have been structurally characterized, let alone the high pressure phases. However, varying permittivities, as for cyclopentanol, have never been observed for the other compounds. Therefore the ODIC phases so far studied are supposed to possess likely cubic structures.

Contrary to the statement of the preceding chapter large enthalpy changes are associated with the solid III–II transition of neohexanol, although the permittivity remains low (Edelmann *et al.* 1991b). The pronounced thermodynamic changes are usually characteristic for an order–disorder transition. It is possible that the transition indeed yields a disordered phase that is not visible dielectrically, due to uniaxial rotations about an axis parallel to the dipole moment in solid II. On the other hand, the enthalpy changes may be small, though the permittivity increases considerably, e.g. for the solid III–II transitions of cyloheptanol (Poser *et al.* 1985). This is probably connected with difficulties to crystallize the substance. It was found that the II–III transition is very sluggish on cooling. In fact the low temperature phase is supposed to be disordered due to a spectroscopic study (Sciesinska *et al.* 1990). Also for cyclooctanol a new phase has been recently established that should be disordered due to a thermal conductivity study (Andersson *et al.* 1990), but shows only low values for the permittivity (Forsman *et al.* 1991). Note that Andersson gives a different notation for the sequence of phases than Edelmann *et al.* (1987).

Permittivities for neohexanol and some cyclic alcohols ranging from C_5 to C_8 are plotted in figure 8. In general ε increases at the freezing temperature for ODIC phases, except for cyclohexanol, where rather a decrease is observed (Pingel *et al.* 1984, Shinomiya 1990). If more than one ODIC phases occur, we observe for the cyclic alcohols a further increase in ε at each phase transition with increasing pressure, contrary to the non-hydrogen-bonded representatives, see figure 5. In this respect the dielectric behaviour resembles the ice phases, see figure 7.

Because the slope of the phase transition lines is in general positive, decreasing temperature or increasing pressure leads to the same sequence of the phase transitions, and correspondingly to the same positive or negative changes in any physical property. However, in the case of neohexanol the solid I–IV transition has a negative slope (see figure 3). Therefore the sequence of phases occurring at decreasing temperature may be 'liquid, solid IV, and I' (e.g. at 200 MPa), where positive changes in the permittivity are observed, similar to the cyclic alcohols. But with increasing pressure we may pass the phases 'liquid, solid I, and IV' (e.g. at 263 K), and we observe a decrease in ε at the solid I–IV transition, similar to the examples of figure 5. Obviously neohexanol exhibits a peculiar phase behaviour and the reader is referred to Edelmann (1991) for further details.

The high permittivities for the liquid and ODIC phases result in large values for the Kirkwood g factor about 3, reflecting the strong correlations due to the hydrogen bonding. However, the temperature dependence of ε cannot be described with the Curie–Weiss law, as was found for ice VI. As for the non-hydrogen-bonded substances we can compare the derivatives $(\partial \log g/\partial \log \rho)_T$ and $(\partial \log g/\partial \log T)_\rho$. For the

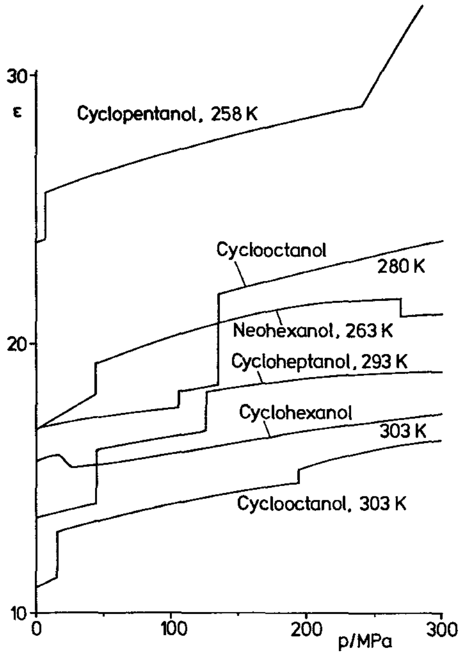
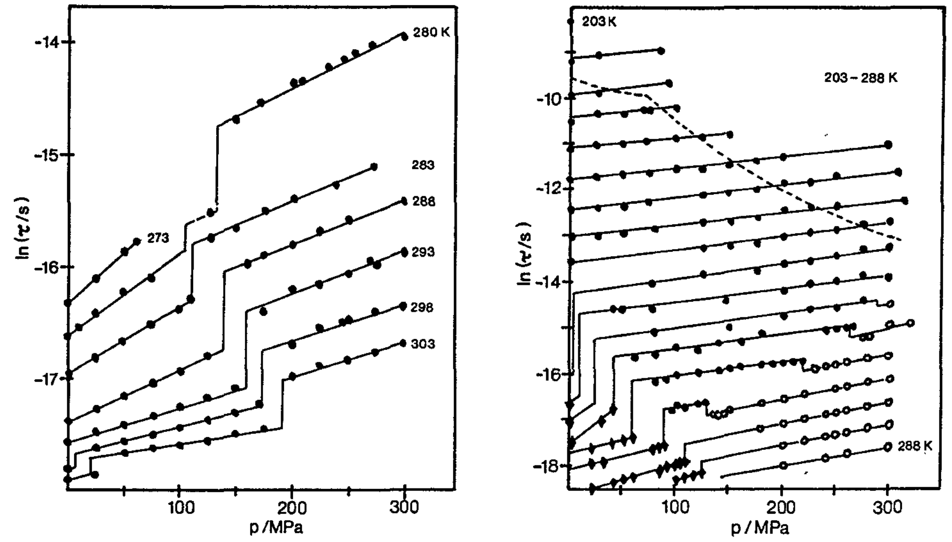


Figure 8. Permittivity of cyclopentanol, cyclohexanol, cycloheptanol, cyclo-octanol and neohexanol at different temperatures and pressures (Würflinger 1982, Pingel *et al.* 1984, Poser *et al.* 1985, 1988, Edelmann *et al.* 1991b). The lower pressure step is always referred to the freezing, apart from cyclo-octanol at 280 K. All other steps concern transitions between different ODIC phases.

hydrogen-bonded substances the g factor is much more temperature dependent under isochoric conditions (Pingel *et al.* 1984, Edelmann *et al.* 1991b).

The cyclic and branched alcohols studied exhibit strong dielectric absorptions at significantly lower frequencies than the non-hydrogen-bonded compounds discussed above. The dielectric relaxation time is of the order of 10^{-8} s near the melting temperature, that is three orders of magnitudes slower, and can therefore be measured with standard bridge methods, e.g. using a Hewlett Packard 4192 impedance analyser (up to frequencies of 13 MHz). In general the loss curves have been fitted to the equations of Havriliak–Negami, to gain the relaxation strength $\varepsilon - \varepsilon_\infty$, and Jonscher for the evaluation of τ. For details see Würflinger (1991) and references therein. Relaxation times τ for cyclo-octanol and neohexanol are plotted in figure 9. The steps of τ at each phase transition are similar to the trends observed for the static permittivity, that is an increase with rising pressure for cyclo-octanol. This behaviour is partly different from the ice phases where τ decreases at the I–III or the V–VI transition, see figure 7. Different relaxation times have been attributed to changing hydrogen bond strengths, the strength decreasing with increasing pressure (Wilson *et al.* 1965).

Activation parameters are collected in table 2 which compare with the results for the ice phases. However, the relaxation times for the alcohols are significantly shorter. This is probably connected with the fact that a H_2O molecule may be hydrogen bonded to four neighbours, whereas only two are involved in the chain-like structures of the alcohols. In this context the investigation of solid methanol is particularly interesting,

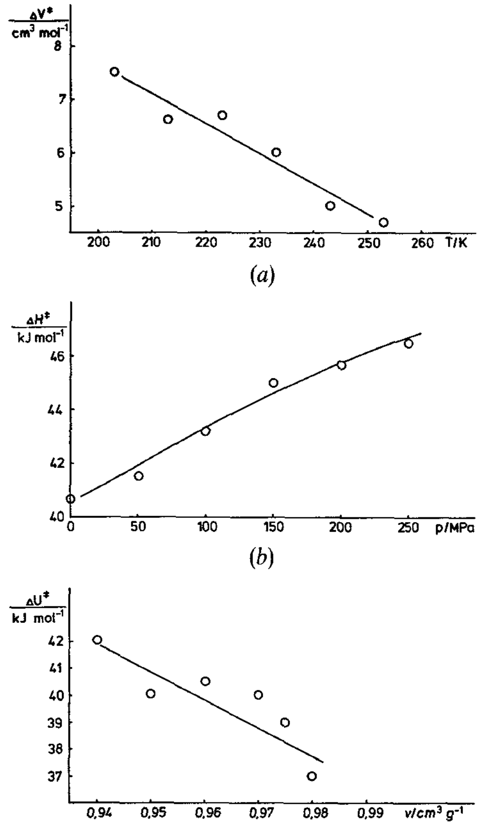


(*a*) (*b*)

Figure 9. Dielectric relaxation times for (*a*) cyclo-octanol (Poser 1987) and (*b*) neohexanol (Edelmann *et al.* 1991b) as a function of pressure for different temperatures (in steps of 5 K for neohexanol). The data beyond the dashed line correspond to the supercooled or superpressed solid I phase of neohexanol.

because its low molecular mass places it closest to water. In fact methanol exhibits several solid phases. The high-temperature β phase has been designated as a disordered one, due to dielectric, nuclear magnetic resonance (NMR), Raman and i.r. studies (Pellegrini *et al.* 1973, Torrie *et al.* 1989, and refs. therein). But it should be noted that the orthorhombic structure of the β phase is very unusual for an ODIC phase. Furthermore, inspecting the dielectric results (Davidson 1957, Ledwig *et al.* 1982) in more detail, one notices permittivities about 5 for frequencies at 100 kHz. Dispersion processes are observed at considerably lower frequencies and may arise from crystal inhomogeneities and polarization at the interfaces between solid and liquid regions. It has been shown previously that small contaminations of water significantly influence the phase behaviour of methanol and pretend the onset of a second transition that does not exist (Landau *et al.* 1977).

The activation enthalpies are appreciably higher than for the non-hydrogen-bonded representatives mentioned above, but the activation volumes are of similar low magnitude (for a comparison of literature data see Pingel *et al.* (1984)). Therefore the reorientation of bulky associates can be disregarded (Scaife 1976). The small activation volumes yield also small differences between $\Delta H^{\#}$ and $\Delta U^{\#}$ (see equation (20)). In fact, large values for the isochoric activation energy seem to be typical for specific interactions. For some alcohols also the pressure dependence of the activation enthalpy could be determined. In all cases $\Delta H^{\#}$ increases, showing that the molecular rotation becomes more restricted at elevated pressures. Similarly, $\Delta U^{\#}$ increases with increasing density that has been found for both plastic phases of cyclo-pentanol (Würflinger 1982). Some typical results for the activation quantities of the solid II phase for cyclopentanol are shown in figure 10. However, these plausible trends are not always observed. For instance, a negative pressure dependence of the activation



(a)

(b)

(c)

Figure 10. Activation parameters, (*a*) $\Delta V^{\#}$, (*b*) $\Delta H^{\#}$, and (*c*) $\Delta U^{\#}$ for the solid II phase of cyclopentanol as a function of temperature, pressure, and specific volume (Würflinger 1982).

enthalpy has been found in ultrasonic studies of rotational isomerism of some branched alkanes (Ledwig *et al.* 1987, Walter *et al.* 1992).

Contrary to the ice phases the ODIC phases of the alcohols exhibit strong deviations from a single Debye relaxation, especially cycloheptanol and cyclo-octanol at higher temperatures. Certainly, the different intramolecular motions which are displayed in branched and cyclic alcohols can modify the distribution of relaxation times (Würflinger 1991). The dielectric behaviour of the neoalcohols is much more Debye-like, probably due to the more globular shape of the molecules. This is also confirmed through the very small activation volume for neopentanol (Kreul 1991).

The distribution of relaxation times at lower temperatures can fairly well be described with the Cole–Davidson equation. The lower the temperature and the higher the pressure, the more the Cole–Davidson parameter β decreases, whereas the Jonscher parameter n increases. Similar pressure dependences have been found by Forsman (1989) in the investigation of some supercooled alcohols. It would be interesting to compare the dielectric properties of ODIC and liquid phases in a broader frame, but data for liquids are only available for some branched heptanols (Vij *et al.* 1981, Scaife

1991) and octanols (Johari *et al.* 1969) and some supercooled and glassy systems (Johari 1976, Forsman 1989).

It is a long tradition to relate the dielectric relaxation time to the viscosity for pure and mixed liquid phases (Debye 1929, Hill *et al.* 1969, Smyth 1980, Beine *et al.* 1986, Shinomiya 1989). According to Debye the ratio τ/η is equal to $3V/kT$ that is approximately valid for globular molecules (Hill *et al.* 1969). As was already pointed out, the plastic crystals do not experience serious changes in τ after solidification, although the viscosity is altered by several orders of magnitudes. Certainly the dielectric behaviour of liquid and solid phases in plastic crystals cannot be modelled in the same way, despite their similar dielectric features.

We briefly mention a study of the dielectric properties and molar polarizations of polycrystalline phenol I and II up to 200 MPa (Bertie *et al.* 1977), although its low permittivities disregard solid phenol to belong to an orientationally disordered crystal. This is also confirmed by the observation of large pressure gradients that do not occur in plastic phases (Chew and Chan 1973). Solid phenol is considered to be a hydrogen-bonded phase in which the hydroxyl hydrogen atoms are ordered, unable to change positions readily. Only transient dispersions were observed probably due to Maxwell–Wagner effects.

3.2. *Liquid crystals*

Only a few dielectric studies under pressure are reported for liquid crystals. Sasabe *et al.* (1972) determined dielectrically the pressure dependence of the crystal–nematic transition in p-methoxybenzylidene-p-n-butylaniline (MBBA). However, the slope derived for the crystal–nematic transition line ($dT/dp = 0{\cdot}261\ \mathrm{K\,(MPa)^{-1}}$) is considerably smaller than the value obtained from a high-pressure differential thermal analysis (DTA) study ($0{\cdot}285\ \mathrm{K\,(MPa)^{-1}}$ after Spratte *et al.* (1976)). MBBA was also investigated by Yasuda *et al.* (1984a) who were probably the first to include dielectric absorption measurements at high pressures (up to 600 MPa). They studied the complex permittivity in the metastable solid phase up to 100 kHz. According to normal pressure studies a dielectric relaxation is only observed in the metastable modification (Moscicki *et al.* 1980, Pathmanathan *et al.* 1986). The pressure dependence of the relaxation time yields two different slopes, correspondingly two different sets of activation volumes are derived: values of about $6\ \mathrm{cm^3\,(mol)^{-1}}$ in the low pressure region (below 350 MPa) and $12\ \mathrm{cm^3\,(mol)^{-1}}$ in the high-pressure region, respectively, indicating a change of the relaxation mechanism as a function of pressure. The activation enthalpies increase with increasing pressure (from 35 to $40\ \mathrm{kJ\,(mol)^{-1}}$ at 600 MPa), whereas the activation volumes decrease with increasing temperature, in accordance with equation (22).

High-pressure studies of the dielectric behaviour in ferroelectric liquid crystals have been reported by Yasuda *et al.* (1985) and Ozaki *et al.* (1987). For a general review on ferroelectric LCs see e.g. Beresnev *et al.* (1988). Yasuda *et al.* investigated the chiral smectic C p-decyloxybenzilidene-p′-amino-2-methylbutylcinnamate, DOBAMBC, that is a ferroelectric LC with a second-order smectic A to chiral smectic C transition at 93°C at 1 atm. The complex permittivity normal to the helix axis was measured up to 200 MPa. The Arrhenius activation enthalpy is about $79\ \mathrm{kJ\,(mol)^{-1}}$ in the Sm-C phase at atmospheric pressure, increasing approximately by $0{\cdot}1\ \mathrm{kJ\,(mol)^{-1}\,(MPa)^{-1}}$. Increasing pressure reduces the polarization and changes the tilt angle of the smectic C structure. The authors established also the p, T phase diagram according to which the coexistence region for the smectic-C phase becomes narrower with increasing pressure.

Similar studies have been performed by Ozaki *et al.* (1987) on 2S, 3S-3-methyl-2-chloropentanoic-acid-4′,4″octyloxybiphenylester, 3M2CPOOB, and S-2″-methyl-butyl-4′-n-nonylcarbonyloxy-1,1′-biphenyl-1-carboxylate, 2MBNCBC. The authors report that dielectric anomalies were not influenced by the application of pressure (below 200 MPa).

The just mentioned high-pressure studies were not concerned with the investigation of the dielectric relaxations in nematic phases. To our best knowledge, such high pressure studies on nematic liquid crystalline phases have been recently performed the first time for 4-n-pentyl-4′-cyanobiphenyl, 5CB, (Kreul 1991. Kreul *et al.* 1992, Urban *et al.* 1992a) and 4-trans-4′-n-hexyl-cyclohexyl-isothiocyanato-benzene, 6CHBT, (Urban *et al.* 1992b). In the course of the measurements we decided to reexamine the phase behaviours of 5CB and 8CB, whereas the phase diagram of 6CHBT was not known at all (Hartmann 1992), see figure 11. For 6CHBT two solid–solid transitions have been found. The lower one is strongly dependent on the thermal history and can be shifted up to the S'_{II} curve.

Figure 12 shows an example of the static permittivity of 5CB in comparison with results reported by Lippens (1978). Kreul's (1991) data for $\varepsilon_{\parallel}$ are only slightly less than the data of Lippens who aligned the sample with a magnetic field of 4 kG. Also the dielectric relaxation time for the low-frequency process does not seem to be changed. Therefore we conclude that our dielectric cell is capable of studying reliably high-pressure dielectric properties of at least some specially chosen liquid crystals.

The choice was governed by the requirement that the low-frequency process is slow enough to be sufficiently separated from the high-frequency process. Such a behaviour can be expected for certain nematic liquid crystals whose dipole moment is essentially parallel to the main axis. The low-frequency relaxation is caused by the strongly impeded rotation of the molecule about its short axis, when the molecule must overcome the nematic potential. Rotation about the long axis is much less hindered and therefore detectable in the high-frequency GHz region. In the isotropic phase both processes merge to yield one broad spectrum of relaxation times.

Detailed results will be presented in forthcoming papers (Kreul *et al.* 1992, Urban *et al.* 1992). We only note here some interesting features of these new high-pressure studies. Figure 12 shows the strong decrease of the static permittivity $\varepsilon_{\parallel}$ when approaching the clearing temperature. The same behaviour is observed for higher constant pressures and also for decreasing pressures at constant temperature (Kreul *et al.* 1992). We mentioned in the Introduction a simplified relation derived from the theory of Maier *et al.* (1961): $\varepsilon_{\parallel} - 1 \cong (2S+1)/T$. Using Horn's (1979) data for the order parameter S, we checked this relation for various temperatures and pressures. Whereas the temperature dependence of $\varepsilon_{\parallel}$ is correctly described, the pressure dependence of $\varepsilon_{\parallel}$ is stronger than this relation predicts (Kreul *et al.* 1992).

This finding has stimulated the idea that pressure affects the nematic state differently than temperature, although both thermodynamic quantities are in principle equivalent. It is well established in the literature that the alkylcyanobiphenyls exhibit a local structure that is governed by a monomer–dimer equilibrium (Leadbetter *et al.* 1975, Druon *et al.* 1978, de Jeu 1980, Longa *et al.* 1982). Low permittivities—and hence Kirkwood g factors below unity—are caused by the presence of antiparallel dimers whose concentration changes with temperature and pressure. For a profound discussion one should distinguish between the region immediately below the clearing temperature, where strong changes are observed, and the region far off. In the case of 8CB $d\varepsilon_{\parallel}/dT$ is almost zero at the nematic–smectic transiiton temperature, and $\varepsilon_{\parallel}$

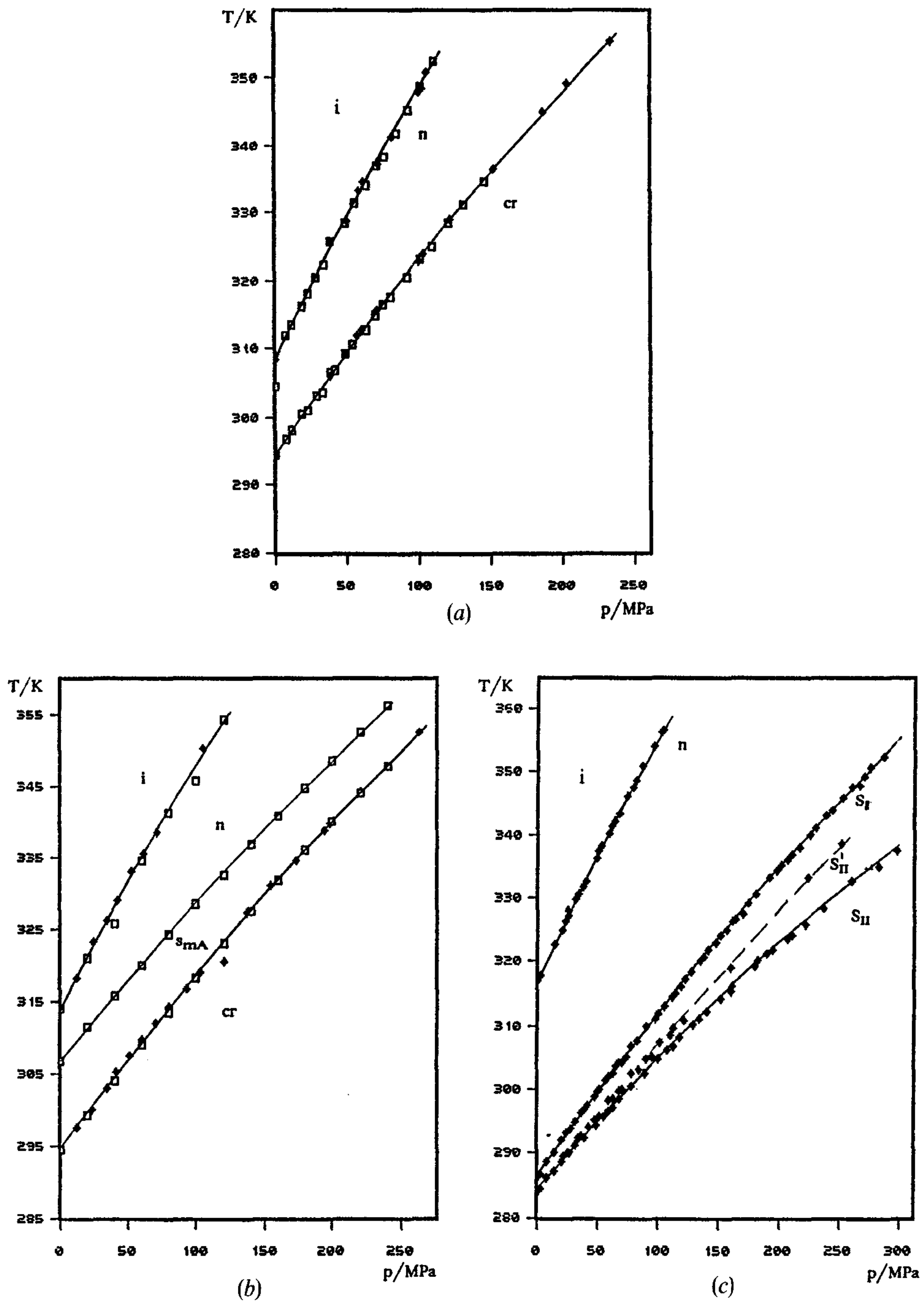


Figure 11. Phase diagrams for (*a*) 5CB, (*b*) 8CB, and (*c*) 6CHBT (Cladis *et al.* 1978, Shashidar *et al.* 1979 and Hartmann 1992).

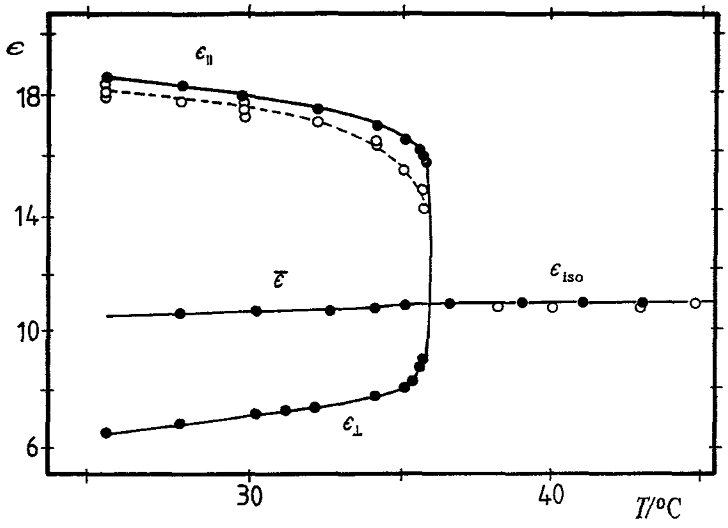


Figure 12. Permittivity of 5CB (Lippens 1978 (◆) and Kreul 1991 (○)).

passes through a maximum in the smectic phase (Thoen *et al.* 1983, Bose *et al.* 1987). Far below the nematic–isotropic transition rather an increasing dimer formation is expected (with decreasing temperature or increasing pressure). To explain the influence of temperature and/or pressure on the monomer–dimer equilibrium remains therefore a delicate problem, let alone the gross assumption to consider the short-range order of being formed by perfectly paired dimers and completely unpaired monomers (Chandrasekhar 1985). In the context we mention also recent theoretical considerations of the molecular structure and reentrant phases in liquid crystals (Indekeu *et al.* 1988) which do not support the simple picture of a monomer-dimer equilibrium.

The low-frequency dielectric relaxation in the nematic phase is very close to Debye. The calculated relaxation times are presented in figure 13 as a function of pressure. The derived activation quantities are plotted in figure 14 showing the very high values both for the energy and volume parameters in the low pressure region. In particular the large activation volumes between 50 and 60 cm^3 (mol)$^{-1}$ are of considerable interest. The decrease of $\Delta H^{\#}$ with increasing pressure is an unexpected result that has never been reported for liquid or plastic crystals. According to equation (22) this finding should be connected with a positive temperature dependence of $\Delta V^{\#}$ that is not confirmed by figure 14. It should be noted, however, that the plots of figure 13 are not straight lines, and therefore the activation volume represents a strongly averaged quantity. The decrease of $\Delta H^{\#}$ and $\Delta V^{\#}$ with increasing pressure could be explained by a breaking of the antiparallel dimers. In the case of 6CHBT no significant changes in $\Delta H^{\#}$ or $\Delta V^{\#}$ with pressure or temperature have been observed (Urban *et al.* 1992b).

High-pressure studies on the dielectric behaviour of LC phases are also a useful tool to examine models of the intermolecular potential. In the Introduction a relation was stated (equation (24)) that connects the nematic potential with the retardation factor. For 5CB at atmospheric pressure $q = 6{\cdot}5$ kJ (mol)$^{-1}$ was obtained in reasonable accordance with similar results for other LCs (Urban *et al.* 1992a). Using literature data for the specific volume and the order parameter S for 5CB it was found that the ratio q/S is practically constant: 11 kJ (mol)$^{-1}$. This proportionality is one of the basic assumptions in the Maier–Saupe theory (Maier *et al.* 1959, 1960). The volume

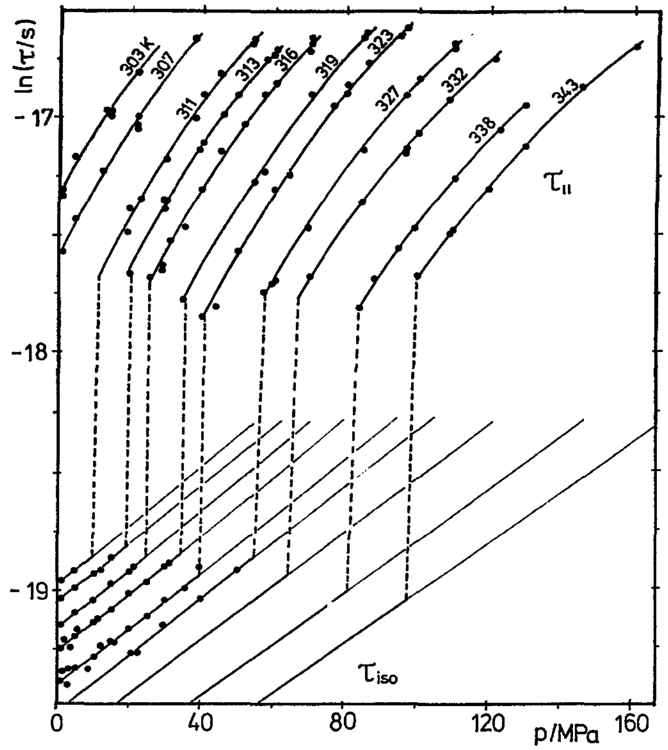


Figure 13. Dielectric relaxation time for 5CB as a function of pressure (Kreul *et al.* 1992). The large step is due to the nematic-isotropic transition.

dependence of the interaction energy can be approximated by a power law ($\simeq V^{-\gamma}$). The same exponent is obtained from the expression: $\Gamma = -(\partial \ln T/\partial \ln V)_S$ (McColl 1972, Luckhurst *et al.* 1979, Emsley *et al.* 1987). Using this formula and other related equations the exponent γ was estimated to be $\approx 5{\cdot}2$ to $5{\cdot}3$ for 5CB, which indicates that also repulsion forces play an important role in the intermolecular potential. For a detailed discussion see Urban *et al.* (1992a).

3.3. *2LC side chain polymers*

Liquid-crystalline polymers which have the mesogenic group in the side chain have attracted many research groups in the last years (for recent reviews see Attard *et al.* (1988), Haase *et al.* (1991)). They are of considerable interest as materials for optical information storage and for their nonlinear optical properties. The study of the pressure dependence of the dielectric behaviours is supposed to give more insight in the understanding of the specific relaxation phenomena occurring in polymers. Heinrich and Stoll (1985b) studied two unaligned LC polyacrylates with p-cyano-phenylbenzoate side groups up to 500 MPa. The dielectric relaxation of the cyano-groups was observed as a separate relaxation process which seemed to be closely related to the glass relaxation. Both processes (α and δ) exhibit the same pressure dependence of the relaxation time.

Moura-Ramos *et al.* (1991) report on the dielectric properties of a smectic siloxane LC polymer having p-cyano-phenylbenzoate groups in the side chain, subjected to pressures up to 150 MPa. The sample had an apparent glass transition temperature

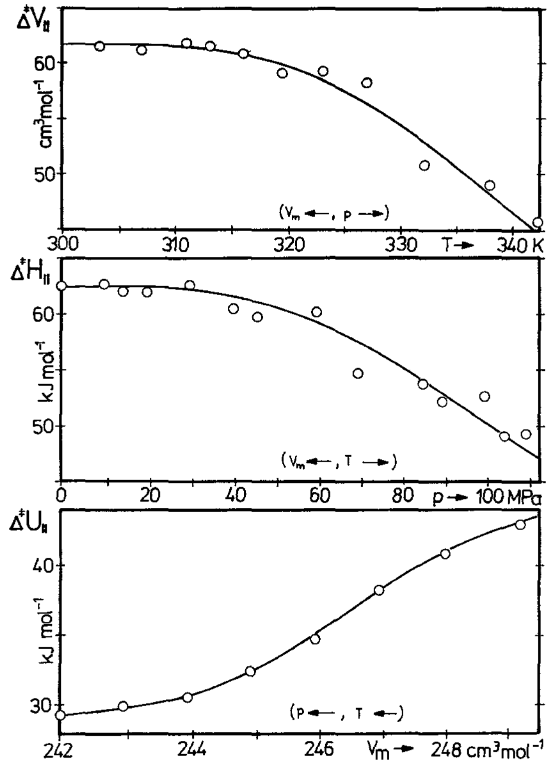


Figure 14. Activation parameters, (a) $\Delta V_{\parallel}^{\#}$, (b) $\Delta H_{\parallel}^{\#}$, and (c) $\Delta U_{\parallel}^{\#}$ for the nematic phase of 5CB as a function of temperature, pressure, and molar volume (Kreul 1991).

of about 274 K and a clearing temperature near 363 K. Also in this study the α and δ processes have approximately the same pressure dependence of $f_{\max}$. The height of the δ peak is markedly increased with pressure. Plots of $(\mathrm{d}T/\mathrm{d}p)_{f_{\max}}$ (see equation (23)) give parallel lines, contrary to amorphous polymers, where a strong increase of the derivative with increasing $f_{\max}$ had been found.

3.4. *Other related materials*

We only mention briefly some other fields of interest such as glasses, polymers and ferroelectrics whose dielectric properties under pressure might be interesting for comparison with plastic crystals. Dunn (1984) gives a short account on general electrical properties at high pressures.

The properties of disordered ferroelectrics, antiferroelectrics, and dielectrics have been comprehensively reviewed by Samara (1990, 1991). The papers highlight the important role of employing pressure for a better understanding of the intermolecular interactions if disordered glassy systems. In particular the properties of various proton glasses, $Rb_{1-x}(NH_4)_xH_2PO_4$, RADP, oxide glasses, $KTa_{1-x}Nb_xO_3$, KTN, other orientational glasses, $KBr_{1-x}(CN)_x$, and semicrystalline polar polymer polyvinylidene fluoride, PVDF, are compared. A remarkable result is the pressure-induced crossover from long-range FE order to glassy behaviour in soft mode systems. A further distinct pressure effect is the strong decrease of the glass transition temperature, T_g, with increasing pressure, and the finite slope, $\mathrm{d}T_g/\mathrm{d}p$, when T_g approaches 0 K in RADP and

KTN. According to the third law of thermodynamics the entropy change accompanying a phase transition should go to zero as $T \rightarrow 0$ K, and consequently the Clausius–Clapeyron equation yields an infinite slope, as is indeed observed for FE and AFE crystals. The finite slope for RADP and KTN comes from the residual configurational entropy in the glassy phase. The temperature dependence of the dipolar relaxation time can be fitted to the Vogel–Fulcher equation. The resulting energy parameters increase with increasing pressure for PVDF, but decrease for RADP and KTN, indicating the vanishing glassy state at high pressures.

Suppressing and generating of glassy states in ferroelectrics induced by pressure is also reported by Roth *et al.* (1989). The influence of hydrostatic pressure on the polarization dynamics of order–disorder ferroelectrics was studied by Petersson *et al.* (1980). Matsushige (1989) reports on pressure effects on phase transitions in ferroelectric polymers. High-pressure X-ray and Raman scattering studies, differential thermal analysis, and dielectric studies have been performed as well. Mroz *et al.* (1988) measured the dielectric properties of TGS, and LATGS single crystals under high pressure.

Hampton *et al.* (1989) and Collier *et al.* (1989) report on the pressure dependence of the dielectric constant of vitreous materials. In particular the permittivity of tellurite and samarium phosphate glasses has been studied, whose pressure dependence is positive in contrast to the behaviour of crystalline insulators. The general pressure dependence is explained on the basis of the Clausius–Mosotti function by the competing effects of compressibility and the pressure dependence of the polarizability.

Pressure-induced phases are reported in thiourea that exhibits ferroelectricity (Yamashita *et al.* 1990). The pressure and temperature dependence of dielectric properties of squaric acid has been studied (Samara *et al.* 1979, Yasuda *et al.* 1979). At ambient pressure $H_2C_4O_4$ undergoes a second order antiferrodistortive phase transition at about 100°C. The dielectric properties of cholesteryl-2,2,3,3-tetrafluoroproportionate (CTFP) that exhibits a series of phase transitions, were measured up to 500 MPa (Yasuda *et al.* 1984b). The dielectric relaxation in phase II yielded activation enthalpies of about $28\,\mathrm{kJ\,(mol)^{-1}}$ at atmospheric pressure, which increase with increasing pressure, and activation volumes of about $15\,\mathrm{cm^3\,(mol)^{-1}}$, which slightly increase with increasing temperature. These dependences do not correspond to equation (22), however, the pressure dependence of $\Delta H^{\#}$ is more intricate in that $\Delta H^{\#}$ first rises gradually and above 300 MPa much more strongly.

4. Concluding remarks

Contrary to the ice phases and ionic solids, relatively little is known about the structural and dynamic properties of plastic and liquid crystalline phases of molecular crystals at elevated pressures. But their investigation would be very deserving, because plastic and liquid crystals are mesophases whose properties lie intermediate between common isotropic liquids and ordered solids. They represent simple model systems for the investigation of phase behaviours, orientational and translational disorder, and dynamic properties in condensed phases. ODIC phases can also be supercooled to yield glassy crystals (Suga *et al.* 1980, Suga 1985) which correspond to orientational glasses (Loidl 1989, Höchli *et al.* 1990). Many representatives are of simple chemical structure that facilitates the employment of computer simulations, such as molecular dynamics (Cicotti *et al.* 1986, Ehrenberg *et al.* 1992).

The wealth of polymorphism that is exhibited in many molecular crystals is far from being well understood. In this paper we presented a small section of some dielectric properties associated with the phase transitions. For instance the changes in the permittivity and the dielectric relaxation time at the phase boundaries revealed some similar trends. For the hydrogen-bonded systems (with some exceptions for the ice phases and neohexanol) ε and τ increase at each phase transition with increasing pressure or decreasing temperature. Also the activation parameters of the alcohols studied and the ice phases agree to a very large extent. Hydrogen bond statistics have been applied for the ice phases and related ferroelectric crystals (Perram 1976, Parsonage *et al.* 1978), but for the solid alcohols, at least for the high-pressure phases, the necessary structural information is very scarce. The high permittivities and large g factors observed for some ODIC phases link them to ferroelecrric systems, although the temperature dependence does not exhibit the characteristic features. The possibility to vary their molecular mass places them intermediate between simple flexible molecules and more complex polymer systems (Shablakh *et al.* 1983). For the non-hydrogen-bonded polar ODIC phases both the relaxation times and the activation enthalpies differ considerably from the alcohol phases, however, again the changes at the melting transition are very small.

The application of pressure has turned out to be particularly relevant, in order to probe the variation of the intermolecular distance. It is indispensable to distinguish between the different influences of volume and temperature for any discussion of the intermolecular potential. Therefore it is very important to know the equation of state as well that enables one to discriminate between isochoric temperature changes and isothermal density changes. This has been demonstrated in the context of the Kirkwood g factor. A strong temperature dependence was found for hydrogen-bonded substances, whereas for non-hydrogen-bonded systems a strong density dependence of the g factor was characteristic (Pingel *et al.* 1984).

The high-pressure studies of some nematic crystalline phases have yielded activation parameters that show peculiar pressure and temperature dependences. The very large activation volumes of about $50\,\mathrm{cm}^3\,(\mathrm{mol})^{-1}$ are not observed for the plastic crystals whether they are hydrogen bonded or not. Also for the other examples mentioned above (metastable phase of MBBA and the incommensurate phase II of CTFP) considerably smaller activation volumes have been found. Although the activation enthalpies are of similar magnitude for nematic LCs and hydrogen bonded plastic crystals, quite different pressure dependences have been found. The zero or even negative pressure dependence of the activation enthalpy observed for nematic phases is quite unusual. In the case of available P, V, T data the volume dependence of the activation energy can be determined, yielding an opposite behaviour for plastic (Würflinger 1982) and liquid crystals (Kreul *et al.* 1992), see figures 10 and 14.

The usefulness of the knowledge of the equation of state was also demonstrated in the discussion of the volume dependence of the intermolecular potential and the retardation factor for 5CB (Urban *et al.* 1992a). Unfortunately P, V, T data are only exceptionally reported for plastic and liquid crystals. Also high-pressure structural information is in most cases not available for the many pressure-induced phases detected in the last few years. These omissions as well as the peculiar features of the mesophases remain a challenge to further experimental and theoretical research.

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