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Conductivity processes in deuterated betaine phosphate_{1-x}betaine phosphite_x mixed crystals

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Abstract. Studies of the electrical conductivity in solid solutions of the mixed crystal system of deuterated antiferroelectric betaine phosphate (DBP) and ferroelectric betaine phosphite (DBPI) were performed. The dc-conductivity σ_{DC} in the temperature interval between 280 and 400 K is obtained from measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ at frequencies between 1×10^{-2} Hz $< \nu < 3 \times 10^6$ Hz. For all crystals studied an anisotropy of σ_{DC} with respect to two crystallographic directions is found. Moreover, we find a clear dependence of the absolute values of σ_{DC} on the phosphite percentage x , whereas the activation energies calculated from an Arrhenius plot of the quantity $\sigma_{DC}^* T$ against the inverse temperature $1/T$ differ only slightly. For the system DBP₃₀DBPI₇₀ the conductivity results are related to data on the microscopic behaviour of the deuteron exchange derived from two dimensional ²H nuclear magnetic resonance (NMR) exchange spectroscopic measurements. An effective charge carrier density is estimated and discussed with respect to the differences between the conductivity and the exchange behaviour for pure deuterated substances.

1. Introduction

Betaine phosphate (BP; (CH₃)₃NCH₂COOH₃PO₄) and betaine phosphite (BPI; (CH₃)₃NCH₂COOH₃PO₃) are molecular crystals consisting of the amino acid betaine and phosphoric and phosphorous acids, respectively. In both compounds the inorganic components (PO₄ or PO₃ tetrahedra) are linked by hydrogen bonds to form quasi-one-dimensional chains along the crystallographic *b*-axis, as shown by Schildkamp and Spilker and others [1–4]. BP exhibits a ferroelastic phase transition at about $T_{C1} = 365$ K followed by two phase transitions at 86 and 81 K. An antiferroelectric order is established at $T_{C2} = 86$ K [1]. At this temperature the O–H...O bonds order along the one-dimensional chains and the chains are linked antiferroelectrically [4]. With dielectric measurements at T_{C1} a kink-like shape of the real part ε' of the dielectric constant was observed by Albers *et al* [2]. BPI transforms at $T_{C1} = 355$ K into an elastically ordered state and exhibits a ferroelectric order below $T_c = 216$ K [5]. The two almost isostructural compounds form solid solutions at any concentrations [2]. It has been shown that at intermediate concentrations the long-range electric order is suppressed [2] and no spontaneous polarization occurs [6].

Deuteration of hydrogen bonded ferroelectrics leads to significant changes of the dielectric properties. Tadic *et al* [7] found that as a consequence of deuteration the phase transition temperature is shifted to higher values. This isotope effect has already been

studied in deuterated crystals of the betaine family, namely betaine phosphate (DBP) and betaine phosphite (DBPI) by Albers *et al* [8] and Bauch *et al* [9]. The low-frequency dielectric measurements of DBPI showed that the ferroelectric phase transition is shifted up to 297 K [9]. However, for both DBP and DBPI the phase transition temperature T_{C1} stays independent of deuteration. The mixed crystals $\text{DBP}_{1-x}\text{DBPI}_x$ have been studied using dielectric spectroscopy by Hemberger *et al* [10] in particular with respect to the glass behaviour. The obtained experimental data were analysed using the δ -plot recently invented [11], providing evidence for a static freezing transition near 30 K.

So far in the investigation of dielectric properties main attention has been devoted to the low-temperature phase transition. In contrast to this, there have been only a few studies of the temperature interval between 300 and 400 K including the high-temperature phase transition from the paraelectric to the antiferrodistortive phase and the conductivity phenomena in mixed BP/BPI crystals [12]. Recently only pure deuterated substances DBP and DBPI were investigated with respect to their dielectric behaviour in this temperature region [13].

The aim of this paper is to investigate the conductivity properties of $\text{DBP}_{1-x}\text{DBPI}_x$ mixed crystals at higher temperatures in the region of the antiferrodistortive phase transition. Particular interest is devoted to the determination of absolute values and activation energies of the dc-conductivity. The density of possible charge carriers is estimated using first nuclear magnetic resonance (NMR) results on the rate of exchange processes which allows us to draw a microscopic picture of conductivity properties. The idea is to enable a thorough and systematic comparison of conductivity phenomena and chemical exchange processes, the detailed study of which is in progress by means of one- and two-dimensional ^2H NMR experiments.

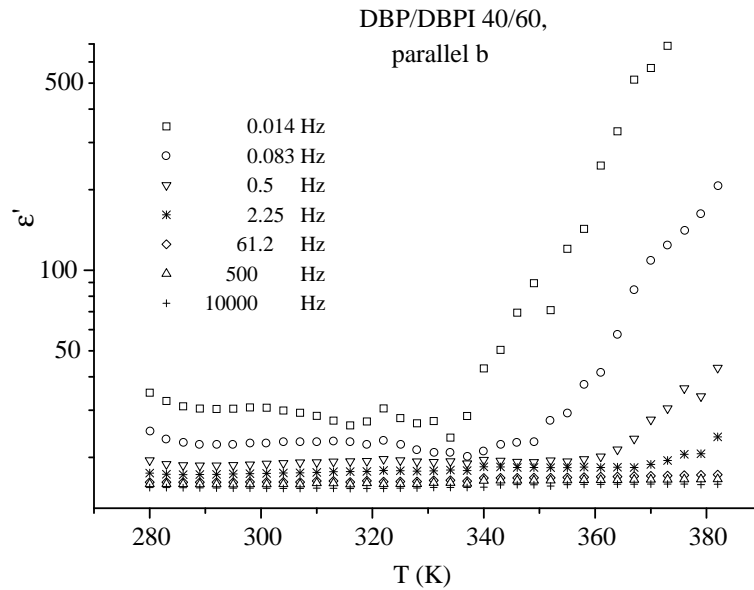
2. Experimental

$\text{DBP}_{1-x}\text{DBPI}_x$ crystals were grown by controlled evaporation from D_2O solution containing betaine and H_3PO_3 and H_3PO_4 . By analogy with DBPI [9] one expects that only protons in O–H...O bonds of inorganic H_3PO_3 and H_3PO_4 groups should be replaced by deuterons. For the dielectric investigations circular shaped slices of 1 mm thickness were cut from the same crystal samples as used for NMR spectroscopic measurements. The crystal slices (area 20 to 30 mm^2) were evaporated with a thin gold layer and electroded with silver contacts.

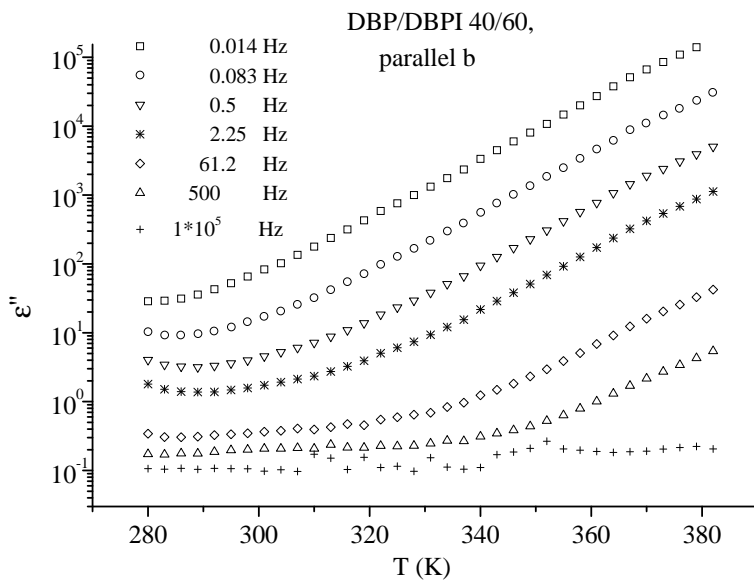
Measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were performed at frequencies from 1×10^{-2} Hz to 3×10^6 Hz and at temperatures between 280 and 400 K using a Schlumberger Solartron 1255 HF frequency response analyser.

3. Results and discussion

Measurements of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were run for the mixed crystals $\text{DBP}_{1-x}\text{DBPI}_x$ with phosphite percentages of $x = 5, 15, 60, 70$ and 85. For each mixed crystal the quantities ε' and ε'' were measured in the direction of the quasi one-dimensional chains (crystallographic b -direction) and perpendicular to them (crystallographic c -direction). Typical dependencies of the real (ε') and imaginary (ε'') part of the dielectric permittivity on temperature T are given in figure 1(a) and (b) for $\text{DBP}_{40}\text{DBPI}_{60}$ (parallel to b -direction). As expected, the values of ε' and ε'' increase with increasing temperature. The curves are given for different frequency values in order to



(a)



(b)

Figure 1. (a) Temperature dependence of the real part of the dielectric permittivity (ϵ') and (b) the imaginary part of the dielectric permittivity (ϵ'') of $\text{DBP}_{40}\text{DBPI}_{60}$.

illustrate that conductivity phenomena play a more significant role at lower frequencies and higher temperatures. At the lowest frequencies used (see $\nu = 0.014$ Hz) the quality of the measured data is influenced by contact effects, since the charge carriers may assemble round the electrodes. In figures 2(a) and (b) typical graphs of ϵ' and ϵ'' against frequency ν for temperatures T of 310 and 385 K are shown for $\text{DBP}_{30}\text{DBPI}_{70}$. It is evident that for frequencies below 1 Hz a distinct increase in both ϵ' and ϵ'' values occurs. For derivation

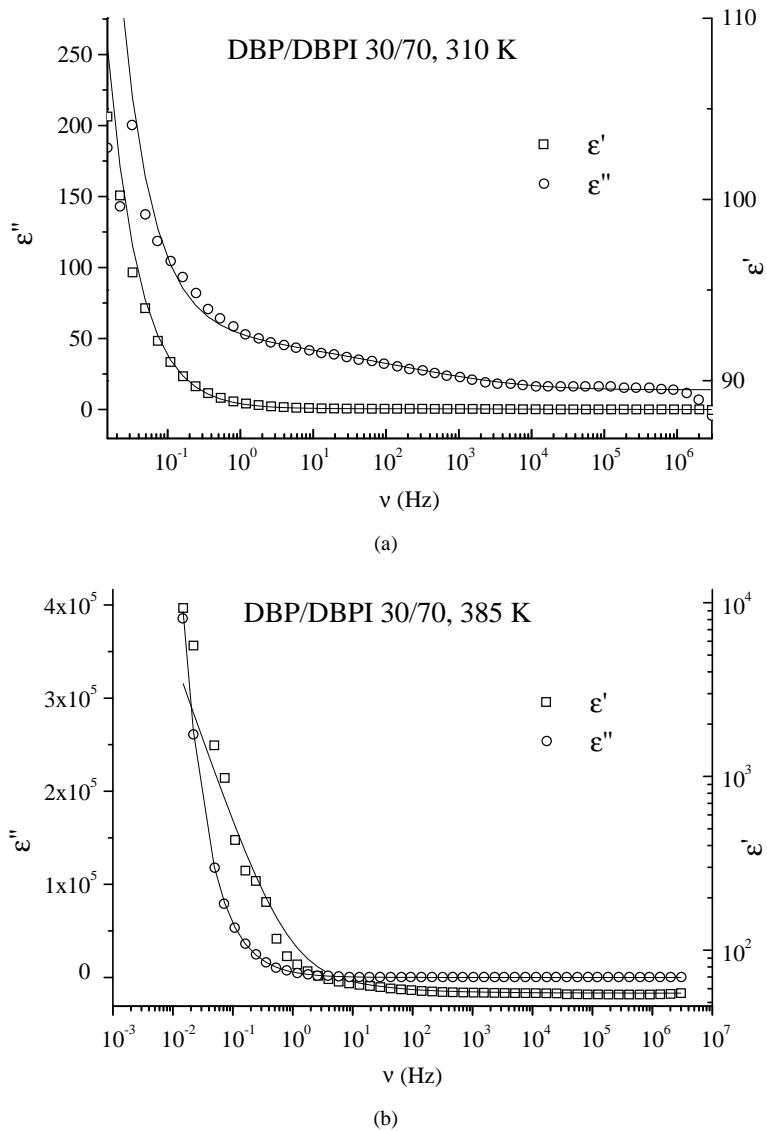


Figure 2. Typical dependence of ε' and ε'' on the frequency ν at temperatures (a) $T = 310$ K and (b) $T = 385$ K for DBP₃₀DBPI₇₀. The squares (\square) and circles (\circ) are the experimentally obtained points for ε' and ε'' , respectively, and the lines are the result of Havriliak–Negami fit (equation 4).

of the dc-conductivity the slope of ε'' is of particular interest. Therefore, in the following we will mainly concentrate on the evaluation of ε'' , because we focus on conductivity phenomena as derived from this quantity.

From the analysis of the ε'' curves (which are typical for all mixed crystals under study) the following conclusions can be drawn. At lower temperatures the slope of ε'' is determined by two processes, namely a conductivity (wing of ε'' curve) and a relaxation process, whereas at higher temperatures (approximately above 360 K) a pure conductivity wing occurs. This change in the ε'' slope with increasing temperature was found for all

DBP/DBPI mixed crystals. In order to retrieve the dc-conductivity from the measurement data, the presence of relaxation processes had to be taken into account. In addition, contact effects occurred at the lowest frequencies which were applied. These contact effects led to an apparently higher conductivity which does not represent a bulk effect of the crystals. Because we need to have precise conductivity data, however, not being influenced by other effects in order to exclude the uncertainties with which the conductivity data of the pure substances are afflicted [13], several evaluation steps were necessary.

First, it had to be guaranteed that we could in fact calculate the activation energy of the conductivity. In such a case non-interacting charge carriers should be present. For this purpose the electrical modulus $M^*(\omega)$ was calculated according to the expression

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = M'(\omega) + iM''(\omega). \quad (1)$$

Figure 3 shows M' and M'' against frequency for selected temperatures for the system $\text{DBP}_{30}\text{DBPI}_{70}$. The real part (M') of the electrical modulus at low frequencies is zero and represents a lack of restoring force for the charge carriers. With increasing frequency they move over shorter distances, until finally the electric field changes so rapidly that the charge carriers move within the region of their potential energy wells. As a result, M' increases to a maximum asymptotic value changing with temperature, as it can be seen in figure 3.

The spectra of M'' show a symmetric peak situated in the dispersion region of M' . The best fit by taking a Debye-type dispersion formula with one relaxation time τ_σ led to widths of quantities M'' which are typical for exponential behaviour of relaxation of the electric field. This result clearly indicates that we deal with non-interacting charge carriers and that calculation of the activation energy of dc-conductivity is possible according to Arrhenius law.

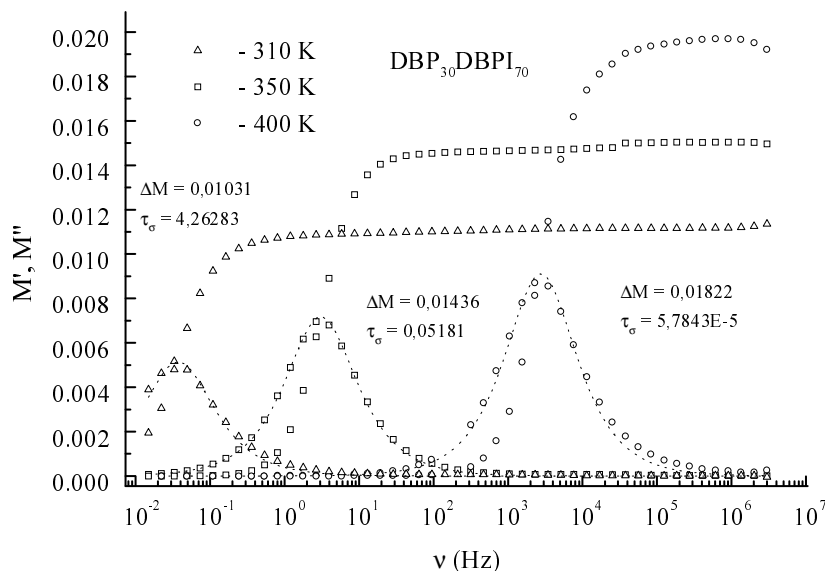


Figure 3. Real (M') and imaginary (M'') part of the electrical modulus against frequency, ν , for $\text{DBP}_{30}\text{DBPI}_{70}$. The values are shown for temperatures 310 K, 350 K and 400 K. Lines are the best fit to a Debye type dispersion formula.

Hence, in a first step the conductivity σ was calculated from ε'' according to

$$\sigma = \varepsilon_0 \varepsilon'' \omega \quad (2)$$

where ε_0 stands for the permittivity of the vacuum. The obtained typical results are shown in figure 4 for DBP₃₀DBPI₇₀ for selected temperatures. The dependence of the conductivity on the frequency $\omega/2\pi = \nu$ obeys the well known general formula [14]

$$\sigma = \sigma_{DC} + A \cdot \omega^s \quad (3)$$

with temperature-dependent parameters A and s . The aim of our investigations was to obtain the dc-conductivity σ_{DC} , which corresponds to the plateau in the σ against ν curve (figure 4), whereas the temperature dependence of the second contribution and especially of the exponent s ($s \leq 1$) was not further studied. In principle, σ_{DC} could be directly obtained from the plateau. Whether this plateau is reached or not, strongly depends on the absolute values of conductivity σ and the covered frequency interval. The higher the values of σ_{DC} , the higher the measurement frequency with which the plateau can be reached. In other words, at relatively low values of σ the use of low measurement frequencies down to 10^{-2} Hz is inevitable.

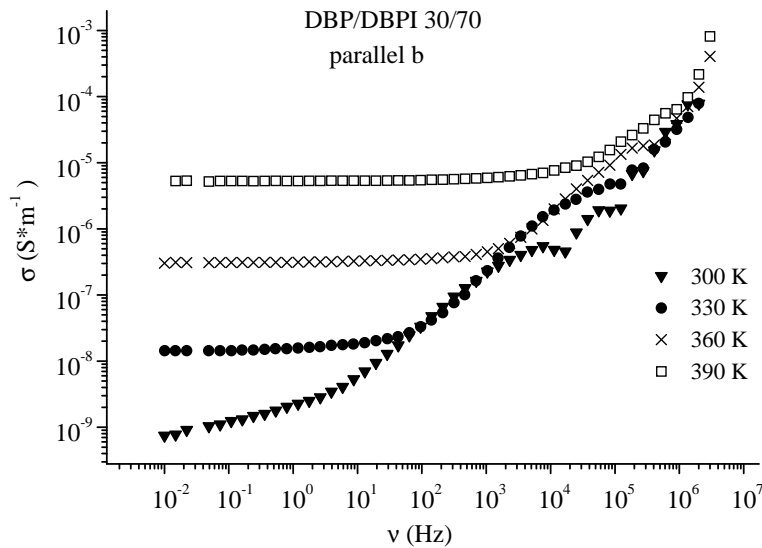


Figure 4. Conductivity, σ , against frequency, ν , for DBP₃₀DBPI₇₀ at different temperatures.

However, as can be seen from figure 4, even with these frequencies the determination of σ_{DC} must fail at least for temperatures below approximately 330 K. At higher temperatures in addition to this, contact effects have to be considered. In fact at higher values of σ_{DC} and low frequencies the measured conductivity is already affected by the sample contacts which is, however, impossible to see from $\sigma(\nu)$. For determination of the possible region of the evaluation of the dc-conductivity another approach must be used. To illustrate the area of the pure bulk conductivity, the complex specific resistance $\rho = \rho' - i\rho''$ at different temperatures was calculated. This is shown in figure 5 where ρ' is plotted against ρ'' . Here the full curve represents bulk conductivity, whereas the points at higher values of ρ' are related to contact conductivity effects.

After finding the temperature interval, where we were able to extract the dc-conductivity, the frequency dependence of ε'' was used to obtain reliable data for σ_{DC} . To obtain results

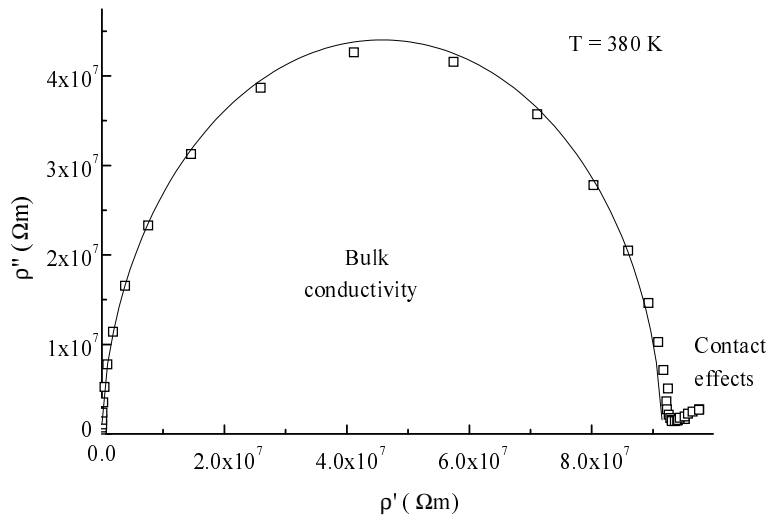


Figure 5. Real part (ρ') against imaginary part (ρ'') of the complex specific resistance at 380 K. The line is the best fit according to the Cole–Cole function.

for the dc-conductivity for all mixed crystals at all temperatures in the range under study, we consequently performed a Havriliak–Negami fit of ε'' according to the equation

$$\varepsilon^*(\nu) = \varepsilon_\infty + \frac{\Delta\varepsilon}{(1 + (i2\pi\nu \cdot \tau)^\alpha)^\gamma} - i \frac{\sigma^*}{\varepsilon_0 \cdot 2\pi\nu} \quad (4)$$

where $\Delta\varepsilon$, τ , ε_∞ and ν denote the relaxator strength, the relaxation time, the contribution of all higher frequency modes to the dielectric permittivity and the measurement frequency, respectively, and α and γ are the Havriliak–Negami parameters. In this equation the quantity σ^* is the complex conductivity $\sigma^* = \sigma' + i\sigma''$, where the real part is the usual conductivity which is split into σ_{DC} and σ_{AC} . (The imaginary part of the conductivity is in charge for the increase of ε' at low frequencies.) The main purpose of our fit was to extract σ_{DC} . The result of this fit is displayed as full curves in figure 2, from where its reliability can be evaluated. σ' changes with the frequency as described by equation (3).

According to this procedure for mixed crystals with $x = 5, 15, 60, 70$ and 85 the dc-conductivities σ_{DC} parallel and perpendicular to the crystallographic b -direction were determined and represented in the form of the plot of $\sigma_{DC} \cdot T$ against $1/T$. In figure 6 σ_{DC} parallel and perpendicular to the b -direction is shown for $\text{DBP}_{40}\text{DBPI}_{60}$. As expected, the absolute values of dc-conductivity in the direction of the chains are approximately one order of magnitude higher than perpendicular to that direction. This anisotropy is found for all mixed crystals studied (not shown here) and corresponds to the findings for pure DBP and DBPI [13].

The activation energies E_A and the pre-exponential factors σ_0 for the conductivity process in $\text{DBP}_{40}\text{DBPI}_{60}$ parallel and perpendicular to the chains were determined to be $E_A = 102 \text{ kJ mol}^{-1}$, $\sigma_0 = 2 \times 10^{10} \text{ K } (\Omega \text{ m})^{-1}$ and $E_A = 97 \text{ kJ mol}^{-1}$, $\sigma_0 = 7 \times 10^8 \text{ K } (\Omega \text{ m})^{-1}$, respectively. These values were obtained by means of fits to Arrhenius law according to

$$\sigma_{DC} \cdot T = \sigma_0 \cdot e^{-E_A/RT} \quad (5)$$

where T stands for the temperature and R is the gas constant.

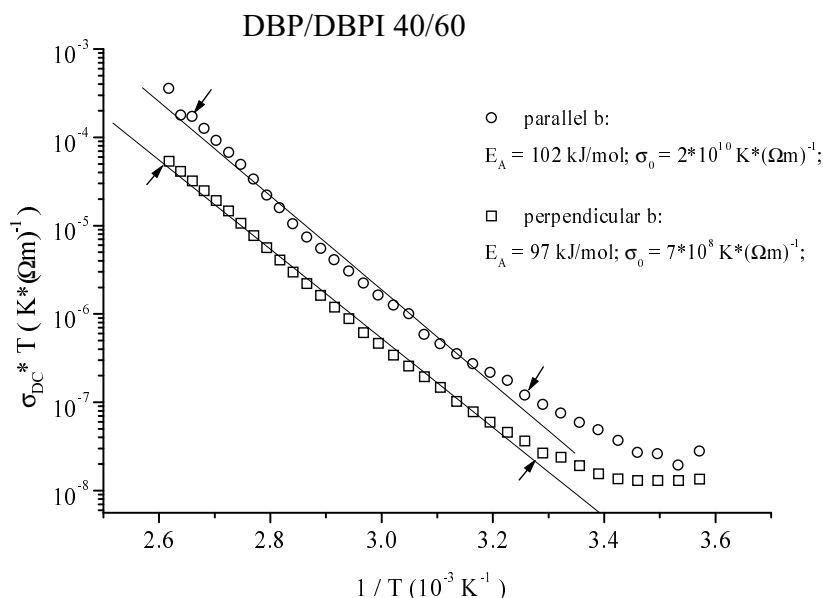


Figure 6. Dc-conductivity against reciprocal temperature for DBP₄₀DBPI₆₀ parallel (□) and perpendicular (○) to the one-dimensional chains. Fitted ranges are indicated by arrows.

Values for E_A and σ_0 (parallel to the b -direction) derived for all mixed crystals studied can be found in table 1, and the respective Arrhenius plots are displayed in figure 7. The error range was estimated to be 5 kJ mol^{-1} for E_A and one order of magnitude for σ_0 . The values for the pure compounds DBP and DBPI (taken from [13]) are added for the purpose of a systematic analysis. This systematic comparative study is also performed by means of figure 7, where the plot of $\sigma_{DC} \cdot T$ against $1/T$ parallel to the crystallographic b -direction is given for four mixed crystals and two pure compounds. In figure 6 at low temperatures deviations from Arrhenius behaviour can be observed. These deviations are caused by inaccuracies in determining σ_{DC} due to the fact that the infrequency dependence of ϵ'' (and σ) the value for σ_{DC} is not reached and much lower frequencies are needed to obtain σ_{DC} (see figure 4).

Table 1. Activation energies E_A and pre-exponential factors σ_0 for the conductivity process for different DBP_{1-x}DBPI_x mixed crystals. E_A and σ_0 are given for dc-conductivity parallel to the crystallographic b -direction. The data for $x = 0$ (DBP) and 100 (DBPI) are averaged values from [13].

x	0	5	60	70	85	100
E_A [kJ mol ⁻¹]	115	110	102	105	101	110
σ_0 [K (Ω m) ⁻¹]	5×10^{11}	3×10^{11}	2×10^{10}	1×10^{10}	2×10^{10}	1×10^{12}

From these experimental results it follows that the absolute values of σ_{DC} decrease with decreasing phosphite percentage x . We observe a gradual change, with the pure compounds having the highest (DBPI) and lowest (DBP) conductivity, respectively. Thus, the differences in σ_{DC} of the pure systems are verified and become clearly visible by the obvious dependence on the parameter x . Moreover, for all crystals, reliable values for

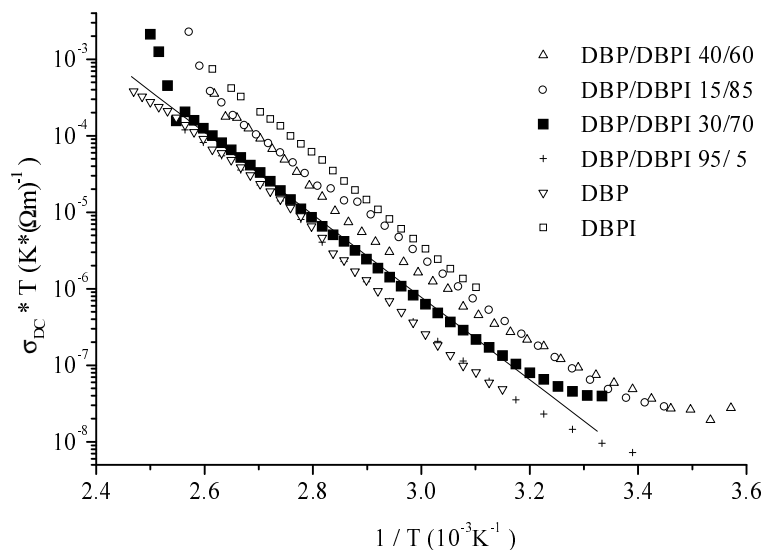


Figure 7. Dc-conductivity against reciprocal temperature for $\text{DBP}_{1-x}\text{DBPI}_x$ with $x = 5, 60, 70, 85$ as well as 0 (pure DBP) and 100 (pure DBPI) parallel to the one-dimensional chains (b -direction). The straight line gives the result of the Arrhenius fit for $\text{DBP}_{30}\text{DBPI}_{70}$.

σ_{DC} are available for the subsequent fit to Arrhenius law according to equation (4). From figure 7 and table 1 it becomes also evident that the activation energies show only slight differences (values between 101 and 115 kJ mol^{-1}). The values obtained for the activation energy are much higher than for temperatures below 100 K [12]. It has already been shown that with increasing temperature the activation energy also increases [15].

Moreover, the question arises whether $\omega_\sigma = 2\pi/\tau_\sigma$ obtained from equation (1) for different crystals of the system $\text{DBP}_{1-x}\text{DBPI}_x$ can be related to the exchange rates obtained by NMR [13]. For different crystals studied ω_σ is always situated at frequencies between 0.03 s^{-1} (at 310 K) and 450 Hz s^{-1} (at 395 K) with a gradual increase towards higher values with increasing temperature. By means of the procedure explained above M'' was calculated for pure DBP and DBPI, for which reliable microscopic data on the exchange rates are already available [13]. However, for both crystals, the exchange rates of which differ by two orders of magnitude, equal values for the frequencies ω_σ were found within the error ranges. This points to a situation where the M'' electric field (conductivity) relaxation time is related to the actual charge carriers only, whereas NMR experiments give a microscopic picture of the whole mobility.

The results of our dielectric measurements clearly show the decrease of the absolute σ_{DC} values with decreasing phosphite percentage in the system $\text{DBP}_{1-x}\text{DBPI}_x$. This conclusion also confirms our earlier findings for pure substances [13] that the conductivity for DBPI is about one order of magnitude greater than for DBP. In strong contrast to the higher conductivity for the deuterated phosphite system, it has been shown unambiguously that the hopping frequencies (deuteron exchange rates) as determined by means of the two-dimensional (2D) ^2H NMR exchange spectroscopy are about two orders of magnitude larger for the DBP crystal than in the case of DBPI [13, 16]. Thus, the higher exchange rate found for DBP does not lead to higher values for the proton conductivity σ_{DC} as compared with DBPI and *vice versa*. As found for pure DBP and DBPI [13] and also

for the system $\text{DBP}_{1-x}\text{DBPI}_x$ the relationship between the measured dc-conductivity σ_{DC} and the chemical exchange (hopping) process of the deuterons is expected to be much more complicated. In order to better understand this problem, we performed an estimation of an effective charge carrier density for the crystal $\text{DBP}_{30}\text{DBPI}_{70}$, using information on the microscopic behaviour available from current 2D ^2H NMR measurements. A detailed discussion of these NMR investigations [17] is beyond the scope of the present work.

Using the approach of a thermally activated charge carrier density $n(T)$, equation (5) is modified to

$$\sigma_{DC} \cdot T = \sigma_0 \cdot e^{-(E_n+E_A)/RT} \quad (6)$$

where E_n stands for the activation energy of the charge carrier density. The pre-exponential value n_0 for $n(T)$ is contained in the expression for σ_0 [13]

$$\sigma_0 = \frac{q^2 a^2}{2k} n_0 \nu \quad (7)$$

where ν and a denote the averaged jump frequency and the jump distance of the deuteron motion, respectively, q is the carried charge and k is Boltzmann's constant.

For a rough estimation of the quantity n for $\text{DBP}_{30}\text{DBPI}_{70}$ a simplifying assumption is adopted that the conductivity originates from deuteron transport along the chains and that the effective carried charge is the elementary charge ($q = 1.6 \times 10^{-19}$ C). The jump frequency ν in equation (7) is interpreted in terms of the pre-exponential factor ($\nu = 1.4 \times 10^{12} \text{ s}^{-1}$), the order of magnitude of which is obtained from the current estimation of the microscopic exchange rates [17]. A value averaged over bond distances in DBP and DBPI molecules for the quantity a of 3.7 Å is used. Based on these assumptions, $n(T)$ was calculated for definite temperatures on the basis of equation (7) using the exchange rate and the dc-conductivity at that temperature and fitted to Arrhenius law. By this means we find the charge carrier density n_0 to be $(4 \pm 4) \times 10^{28} \text{ m}^{-3}$ and an activation energy E_n of about $(30 \pm 5) \text{ kJ mol}^{-1}$. The latter corresponds to the difference in activation energies of the conductivity (105 kJ mol^{-1} , see table 1) and the exchange processes (72 kJ mol^{-1} , [17]), supporting our approach of a thermally activated charge carrier density.

Estimation of the charge carrier density by means of this procedure leads to a value more than an order of magnitude larger than found for DBP and DBPI [13]. Although the precision of this estimation is not sufficient to draw final conclusions, this might point towards the importance of defects for the conductivity process. In fact, whatever model for conductivity mechanisms is considered (e.g. one similar to that for proton conductivity in KDP [18]) one has to deal with the fact that deuterons can only jump and move along the chains when certain defects in the crystallographic structure are present. Then the respective vacancies caused by missing deuterons should move in opposite directions.

Provided that the creation of defects is in fact favoured by the substitution of DBP for DBPI molecules or *vice versa* in the mixed crystals $\text{DBP}_{1-x}\text{DBPI}_x$ and assuming that this process is thermally activated, it gives new hints to the nature of charge carriers. However, we have to be aware that n was obtained by estimation where we merely used the jump frequency ν , which only involves inter-bond jumps, since only these are observable in our NMR exchange experiments. Intra-bond jumps which certainly play a role in the creation of defects and the exchange process are not covered by this technique. (Unfortunately, for temperatures studied in the present work, a direct measurement of the intra-bond jump rate, which has been estimated for instance by Blinc *et al* at low temperatures in the case of deuterated KDP type crystals [19], is not possible.) In connection with this, to explain

the differences in macroscopic and microscopic behaviour as mentioned earlier further influences have to be taken into account. Consequently, two competing effects are supposed to be introduced when replacing DBP by DBPI molecules. The microscopic mobility in its entirety is lowered (lower exchange rates for pure DBPI), but the one-dimensional alignment of the movement is increased (three exchanging sites instead of four, only one of which is not in the chain direction).

In order to refine the approach given previously, a clear separation of the microscopic exchange paths will be necessary which implies the evaluation of various sets of 2D NMR experiments which are not yet available. However, with systematic analysis of conductivity behaviour presented here the uncertainties with respect to macroscopic quantities are excluded and new clues with respect to charge carriers are found.

4. Conclusions

We systematically investigated the electrical conductivity properties of the mixed crystal system $\text{DBP}_{1-x}\text{DBPI}_x$ in the temperature interval between 280 and 400 K including the antiferrodistortive phase transition. Using measurement frequencies down to 1×10^{-2} Hz and applying different evaluation methods for the quantity σ_{DC} we were able to determine σ_{DC} independent of contact effects and the influence of σ_{AC} . A clear and gradual decrease of the absolute values of σ_{DC} with decreasing phosphite percentage was found, whereas the activation energies for the system $\text{DBP}_{1-x}\text{DBPI}_x$ differ only slightly. With different methods we obtained equal values for E_A .

For $\text{DBP}_{30}\text{DBPI}_{70}$ quantitative relations between conductivity and chemical exchange processes are discussed by estimating the effective charge carrier densities n . The temperature-dependent approach for this quantity was confirmed by the difference in the activation energies of about 30 kJ mol^{-1} . Uncertainties with respect to the conductivity in pure substances are excluded, and a systematic comparison with microscopic data from current 2D ^2H NMR exchange spectroscopy becomes possible in order to elucidate the discrepancy between the behaviour of dc-conductivity and exchange rates.

Acknowledgments

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