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Dielectric relaxation behaviour of protonated and deuterated betaine arsenate

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Abstract. This work reports the study of the dielectric relaxation of betaine arsenate (BA) and of strongly deuterated betaine arsenate (DBA92) below room temperature for different values of d.c. electric fields, in the frequency range of 50 Hz–13 MHz. The main contributions for dielectric constant come from low-frequency relaxation modes. Some evidence for the existence of a new antiferroelectric phase in BA was found, stable in a short range of temperatures.

1. Introduction

Betaine arsenate ((CH₃)₃NCH₂COO.H₃AsO₄), here designated by BA, like some other betaine compounds, exhibits interesting dielectric and elastic properties [1–6].

It undergoes a para–ferroelastic transition at $T_{C_1}^H \approx 411$ K. The space group below $T_{C_1}^H$ is $P12_1/n1$ [7]. It undergoes also another structural phase transition at $T_{C_2}^H \approx 120$ K and below this temperature it presents a ferroelectric state with symmetry $P1n1$. Around $T_{C_2}^H$ the dielectric constant displays a broad maximum with values of 10^5 – 10^6 . The pyroelectric effect reveals a very sharp peak at 123 K and a larger and smaller anomaly at 119 K [8]. Under a weak electric field the BA shows hysteresis loops with strong distortions which vanish if an a.c. electric field of high amplitude is applied [9]. In a 5 K temperature range below $T_{C_2}^H$ the coercive field is very low (less than 20 V cm⁻¹) [9]. The hysteresis loop shape is strongly dependent on the frequency of the a.c. voltage. So far the mechanisms underlying the critical behaviour of BA are not completely understood.

For concentration higher than 77%, the deuterium changes drastically the properties of BA, and for a deuterium content of 92% (DBA92) an antiferroelectric phase (AFE) arises between $T_{C_2}^D \approx 162$ K and $T_{C_3}^D \approx 132$ K with symmetry $P12_11$ [10, 11]. Below $T_{C_3}^D \approx 132$ K two ferroelectric phases were identified (FE1 and FE2) [12], both with a space group $P1n1$ [11].

Some of these results have provided evidence for the existence of competitive interactions in the BA_{1-x}DBA_x system [13]. On the basis of these competitive interactions a model was presented to describe the dielectric properties of BA [4].

In this work we have studied the dielectric relaxation of BA and of strongly deuterated BA (DBA92) below room temperature for different values of d.c. electric fields, in the frequency range of 50 Hz–13 MHz. The main contribution to the dielectric constant comes from low-frequency relaxation modes. Some evidence was found for the existence of a new antiferroelectric phase in BA, stable in a short range of temperatures.

2. Experiment

The crystal of BA was grown by controlled evaporation from a equimolar aqueous solution of arsenic acid and betaine. The deuterated compound was obtained by the same method in a solution containing deuterated water. The samples were cut in (001) plates and gold electrodes were deposited by evaporation. We used a closed-cycle helium cryostat for cooling the samples to 30 K. For the automatic measurements, an HP 4192A impedance analyser was used. It is possible to measure the capacitance and the loss factor in the 5 Hz–13 MHz frequency range and under d.c. bias voltage up to ± 35 V.

In the study of the dielectric dispersion, the stabilization of the temperature was better than 0.05 K.

3. Results and discussion

In the analysis of the experimental results we have assumed that the dielectric constant, for different frequencies and at a fixed temperature, can be described by the function:

$$\begin{aligned}\varepsilon^*(\omega) &= \varepsilon(\infty) + \sum_j \frac{\Delta\varepsilon_j}{1 + (i\omega\tau_j)^{\beta_j}} \\ &= \varepsilon'(\omega) - i\varepsilon''(\omega) \quad j = 1, 2, \dots\end{aligned}$$

where $\varepsilon(\infty)$, $\Delta\varepsilon_j$, τ_j and β_j are adjustable parameters: $\varepsilon(\infty)$ dielectric constant for high frequencies; $\Delta\varepsilon_j$ dielectric amplitude, τ_j relaxation time and β_j dispersion coefficient for the j relaxation mode. This model assumes that the modes considered are independent, which is verified when the relaxation frequencies of each mode are very different. The experimental values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are well fitted simultaneously to the function $\varepsilon^*(\omega)$ referred to above.

In figure 1(a) we show the real ($\varepsilon'(\omega)$) and imaginary ($\varepsilon''(\omega)$) parts of the dielectric constant of BA measured in a wide frequency range for some temperatures. In figure 1(b) we can see $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for BA under a d.c. field of 200 V cm^{-1} at different temperatures. The figures 2(a) and 2(b) exhibit $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for DBA92 at zero field and under a d.c. field of 700 V cm^{-1} , respectively. These figures show that the dielectric constants of BA and DBA92 behave in a complex way and the main aspects of their behaviour can be taken into account by assuming the existence of two relaxation modes with dielectric amplitudes strongly dependent on the temperature. One of these modes, here called the high-temperature mode (HT), is relevant in the whole temperature range studied and the other mode, the low-temperature mode (LT), becomes explicit only below $T_{C_2}^H$ in BA and below $T_{C_2}^D$ in DBA92. The behaviours of some of these modes are clearly modified by high enough d.c. fields.

We analyse first the experimental results obtained in BA. In figure 3(a) we can see the dielectric amplitude of the HT mode ($\Delta\varepsilon_1$) and the dielectric amplitude ($\Delta\varepsilon_2$) of the LT mode at zero d.c. field. Both modes present sharp anomalies: the HT mode at $T_{C_2}^H \approx 120$ K and the LT mode at $T_{C_3}^H \approx 110$ K. Above 120 K the dispersive coefficient β_1 is very close to 1.0 (inset of figure 3(b)) which means that BA behaves like a monodispersive system above that temperature, but as soon as the LT mode becomes very explicit, the β_1 values decrease steeply down to 0.2. The dispersive coefficient β_2 related to the LT mode has also a value very different from 1. The relaxation times of the HT (τ_1) and of the LT (τ_2) modes, displayed in figure 3(b), present anomalies that peak at 120 and at 110 K, similarly to the behaviour of $\Delta\varepsilon_1(T)$ and of $\Delta\varepsilon_2(T)$, respectively. The order of magnitude of these relaxation times are very different.

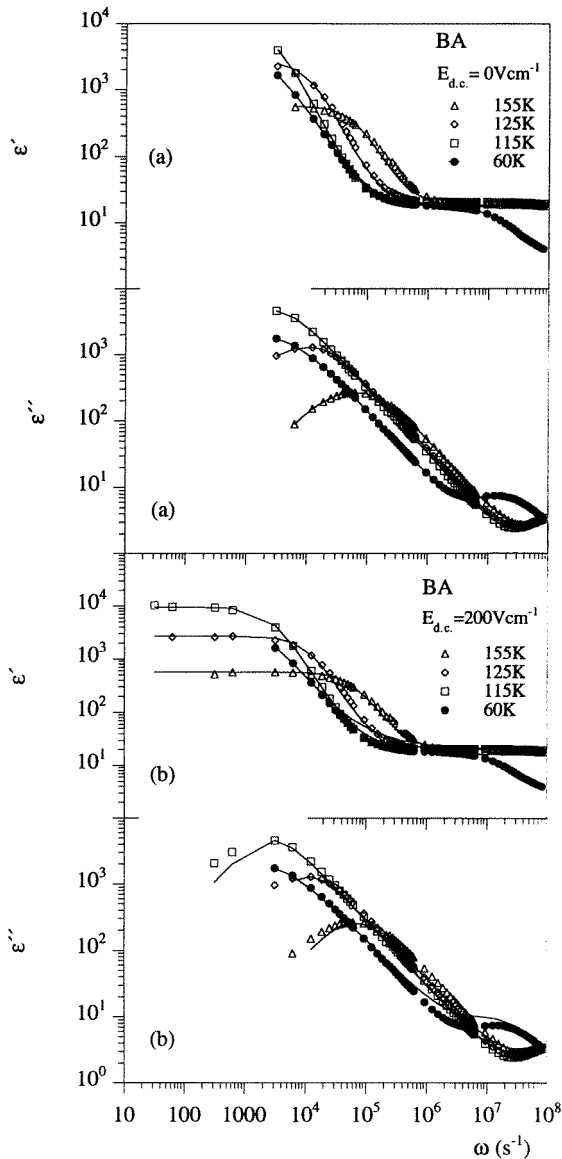


Figure 1. Frequency dependence of ϵ' and ϵ'' of the complex dielectric constant of BA measured under a d.c. electric field of 0 V cm^{-1} (a) and of 200 V cm^{-1} (b) for some temperatures. We used a double-logarithmic representation. The solid lines are calculated using the Cole-Cole model for the complex dielectric constant.

By applying a d.c. field of 200 V cm^{-1} we also observe two modes, but these modes behave in a very different way in comparison with the two previously referred to. As can be seen in figure 4(a) the dielectric amplitude $\Delta\tilde{\epsilon}_1(T)$ of the HT mode presents a very broad anomaly with a maximum that occurs at 115 K and a very weak mode ($\Delta\epsilon_3 \approx 18\text{--}26$) with a maximum at 87 K, visible in the 30–160 K temperature range. The dispersive coefficient $\tilde{\beta}_1$ is very close to 1.0 above 115 K and approximately 0.95 below this temperature and the

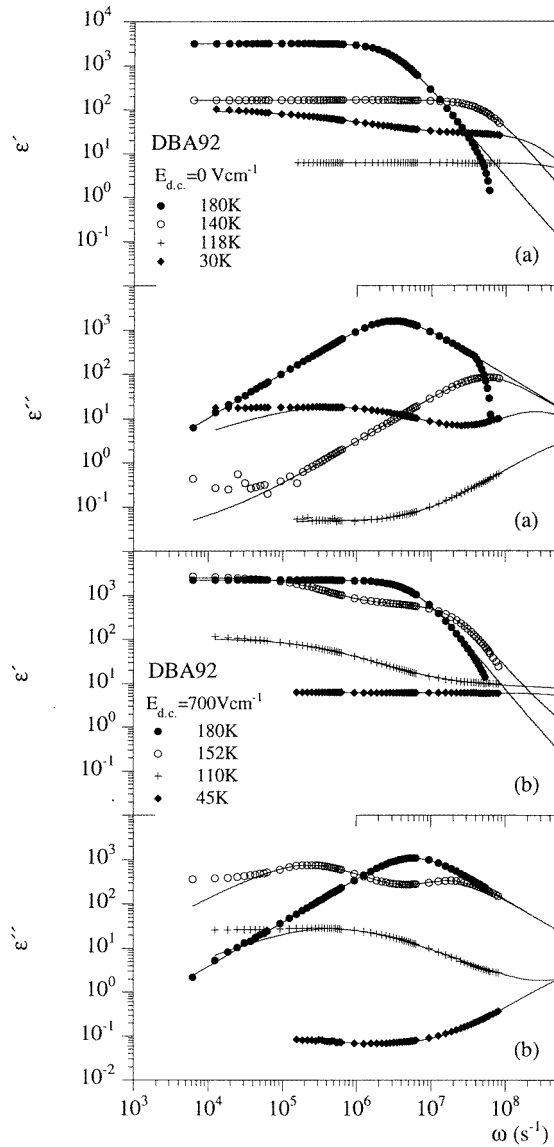


Figure 2. Frequency dependence of ϵ' and ϵ'' of the complex dielectric constant of DBA92 measured under a d.c. electric field of 0 V cm^{-1} (a) and of 700 V cm^{-1} (b) for some temperatures. We used a double-logarithmic representation. The solid lines are calculated using the Cole-Cole model for the complex dielectric constant.

coefficient β_3 is about 0.8 and goes down to 0.4 near 100 K, as can be seen in the inset of figure 4(b). The HT mode relaxation time $\tilde{\tau}_1$ presents a broad anomaly while the weak mode has a much smaller relaxation time (τ_3) with a sharp maximum at 95 K, approximately (figure 4(b)).

Now let us see the results concerning DBA92. In figure 5(a) and 5(b) are depicted the dielectric amplitude ($\Delta\epsilon_1$) of the HT mode and the dielectric amplitude ($\Delta\epsilon_2$) of the LT mode at zero field and for the d.c. fields of 400 V cm^{-1} and of 700 V cm^{-1} .

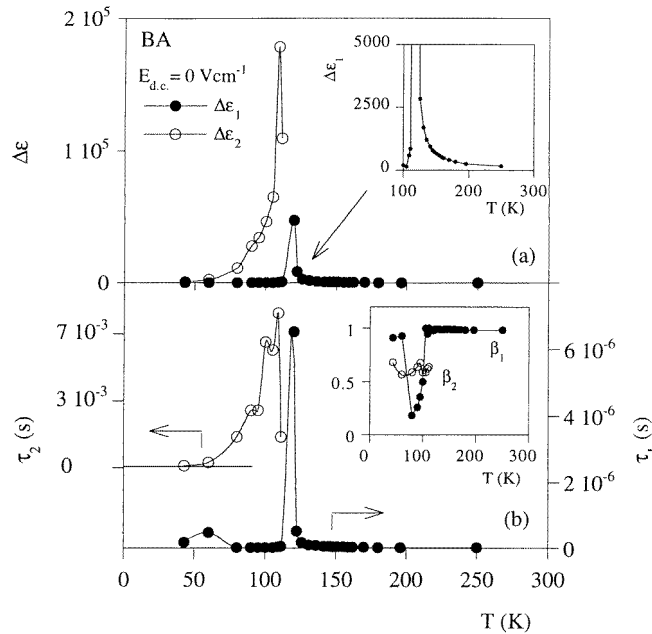


Figure 3. Dielectric amplitudes (a) and relaxation times (b) of the HT and LT modes in BA, for zero electric field. The inset shows the behaviour of the dispersive parameter β as a function of the temperature for the two relaxational modes.

Above $T_{C_2}^D$, the main contribution for dielectric constant comes from the HT mode which is quite insensitive to a d.c. applied field. $\Delta\varepsilon_1(T)$ presents a rather sharp anomaly with a maximum at 168 K and this temperature corresponds to the onset of the antiferroelectric phase. $\Delta\varepsilon_1$ increases slightly as the field increases. Figure 6(a) displays the relaxation time (τ_1) as a function of the temperature for different values of the d.c. field. $\tau_1(T)$ is quite similar for $E = 0 \text{ V cm}^{-1}$ and for $E = 400 \text{ V cm}^{-1}$, but decreases a bit for $E = 700 \text{ V cm}^{-1}$. All the curves present an anomaly with a maximum at 168 K, in good agreement with the behaviour of $\Delta\varepsilon_1(T)$. Within the experimental errors, the dispersion coefficient β_1 is 1.0 as can be seen in the inset of figure 6(a). This result means that the HT mode in DBA92 is a Debye type mode.

At zero field (figure 5(b)) the contribution ($\Delta\varepsilon_2$) of the LT mode for the dielectric constant becomes very explicit below $T_{C_3}^D \approx 132 \text{ K}$, i.e., the onset of the FE1 phase. As long as the field increases the temperature range of stability of the LT mode becomes larger and, at variance with the HT mode behaviour, $\Delta\varepsilon_2$ increases significantly, when the field increases. As can be seen in the inset of figure 6(a), the dispersive coefficient β_2 of the LT mode reveals a strongly polydispersive type behaviour. At zero field and for $T_{C_4}^H \approx 87 \text{ K}$, $\beta_2(T)$ presents a step that bears witness to the FE1–FE2 phase transition. The relaxation time (τ_2) of the LT mode increases with the field, as depicted in figure 6(b), and its maximum value occurs at a temperature that increases with the field.

The interpretation of the experimental results in DBA92 is straightforward. Below and above $T_{C_2}^D \approx 162 \text{ K}$, the HT mode appears as a clear manifestation of antiferroelectric interactions mainly related to deuterons and its close environment. An antiferroelectric state must be quite insensitive to d.c. electric fields below the critical field and this was observed experimentally. The association of the antiferroelectric state with deuterons

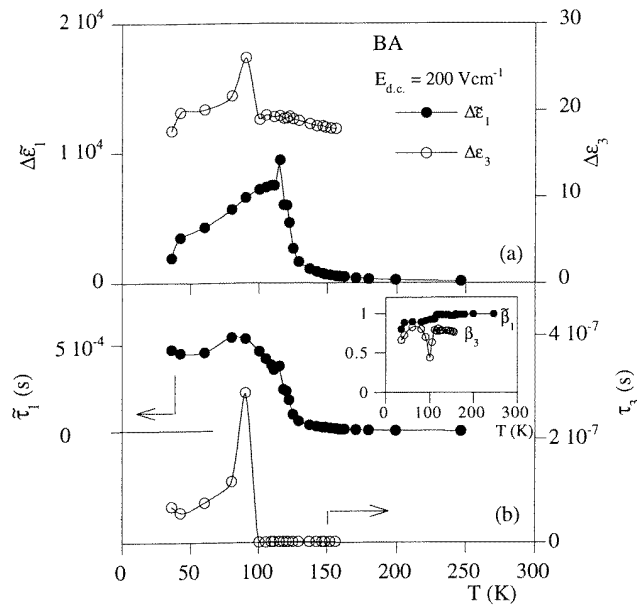


Figure 4. Dielectric amplitudes (a) and relaxation times (b) of the HT and LT modes in BA, for an electric field of 200 V cm^{-1} . The inset shows the behaviour of the dispersive parameter β as a function of the temperature for the two relaxational modes.

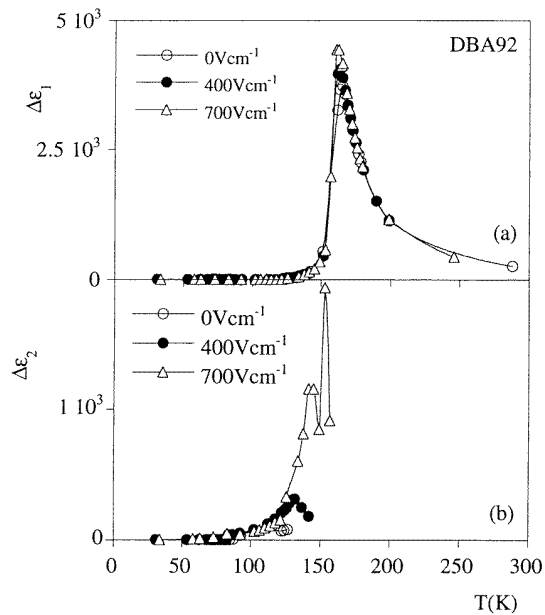


Figure 5. Dielectric amplitude for the HT mode (a) and for the LT mode (b) in DBA92 for zero field and for different values of the electric field.

stems mainly in the large upshifting of the critical temperature $T_{C_2}^H$ of BA by deuteration ($T_{C_2}^H \approx 120 \text{ K} \rightarrow T_{C_2}^D \approx 162 \text{ K}$). It is then rather plausible to assume that in the

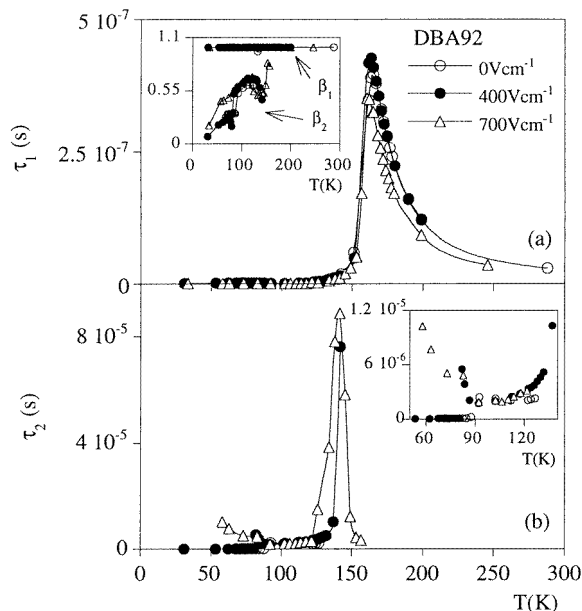


Figure 6. Relaxation times for the HT mode (a) and for the LT mode (b) in DBA92 for zero field and for different values of the electric field. The inset of (a) shows the behaviour of the dispersive parameter β as a function of the temperature for the two modes. The inset of (b) shows a detail of the relaxation time τ_2 .

antiferroelectric phase the deuterons are ordered in an antiferroelectric state along the c -axis. The dispersive coefficient β_1 is very close to 1.0 providing evidence for the existence of uniform potential barriers in the relaxation processes.

Below $T_{C_3}^D \approx 132$ K another mode becomes very explicit at the onset of the FE1 phase of DBA92 and many aspects of its behaviour, namely the dielectric amplitude, the dispersion coefficient and the relaxation time are clearly modified by a d.c. field. So this mode would be related to ferroelectric interactions which are enhanced by a d.c. field, coexisting with antiferroelectric ones. The units involved in this mode exhibit a large pattern of relaxation times which are clearly associated with energy barriers split into more or less separated valleys relevant in the relaxation processes. The dynamics observed could be related to some disorder arising as a consequence of the coexistence of antiferroelectric and ferroelectric interactions. The deuterons shift the temperature from $T_{C_3}^H \approx 110$ K to $T_{C_3}^D \approx 132$ K which represents a smaller increase than in the situation related to the HT mode. So, the polarization in the FE1 phase could be mainly originated by a deformation of AsO_4^{3-} units and of the betaine molecules, with less participation of deuterons. In fact the Raman study of the bending and of stretching modes of AsO_4^{3-} as a function of the temperature displays very explicit anomalies around $T_{C_3}^D$, providing evidence for changes in the angles and in the distances of the AsO_4^{3-} units at the AF-FE1 phase transition [11]. Close to $T_{C_2}^D$ the internal modes of AsO_4^{3-} behave, in general, in a smooth way.

From the arguments developed before, it is rather tempting to conclude that the behaviour of the HT mode is mainly determined by units that include deuterons, while the LT mode behaviour is mainly originated by the AsO_4^{3-} relaxations and may be coupled to betaine molecule displacements.

This analysis gives strong support to the *ansatz* in a previous work [12] where it was assumed that the FE1 phase does not appear as a consequence of the reversal of dipolar momenta of one of the two sublattices of the antiferroelectric phase but would be due to the ordering of some other dipolar momenta. Therefore, in the FE1 phase it would coexist an antiferroelectric ordering of deuterons and a ferroelectric ordering of the electric dipole momenta of AsO_4^{3-} and of betaines. The coexistence of these interactions would make the DBA92 very 'soft' in the FE1 phase and could explain its dielectric behaviour. The results obtained present also clear evidence for the FE1–FE2 phase transition around 80 K in DBA92 (inset of figure 6(b)). At this temperature BA presents also an anomalous behaviour in $\Delta\tilde{\epsilon}_1(T)$ and $\tau_3(T)$ as can be seen in figure 4(a) and 4(b).

The complex behaviour of BA can be understood by assuming that the HT mode is also related to antiferroelectric interactions and the LT mode is mainly related to ferroelectric interactions. From figures 3(a) and 3(b) it is obvious that the onsets of the phase transitions associated with the anomalies of $\Delta\epsilon_1$ and of $\Delta\epsilon_2$ do not take place at the same temperature. If the assignment of the HT and the LT modes is correct, this means that a para-antiferroelectric phase transition would occur at $T_{C_2}^H \approx 120$ K and an antiferro-ferroelectric phase transition would take place at $T_{C_3}^H \approx 110$ K. Owing to the small difference of the temperatures $T_{C_2}^H$ and $T_{C_3}^H$, $\epsilon'(T)$ must present a broad anomaly which is in fact verified [9]. At variance, the pyroelectric effect presents two very well defined anomalies at temperatures that differ by some degrees, one very sharp at 123 K and another very broad around 119 K [8]. The main contribution to the polarization arises from the broad anomaly. The very sharp peak could be due to some unbalanced charges in the two sublattices. This hypothesis may explain also the S shaped hysteresis loops observed in BA, above 120 K, and the strong distortions in low a.c. fields displayed below this temperature.

By applying a d.c. electric field of 200 V cm^{-1} the behaviour of the modes changes drastically. We observe two modes, one with a dielectric amplitude reduced by a factor of ten which is not surprising, but the other one with a very abnormal tiny amplitude of 18–26. As this mode presents an anomaly around 80 K and has a very small dielectric amplitude it is expected that this weak mode does not correspond to the LT or the HT modes observed in BA at zero field. It is rather plausible to assume that this mode is a polar mode induced or enhanced by the field. As concerns the HT mode of BA under the field of 200 V cm^{-1} , we can see in figure 4(a) that the dielectric amplitude $\Delta\epsilon_1(T)$ presents a broad anomaly with a maximum at 115 K, in contrast with the sharp anomalies of $\Delta\epsilon_1(T)$ and of $\Delta\epsilon_2(T)$ in BA, at zero field. So we assume that under a field these two modes merge, exhibiting a predominantly ferroelectric character. Under a d.c. field and above $T_{C_2}^H$ the relaxation times of BA present a higher dispersion than the BA at zero field, but below $T_{C_2}^H$ and in contrast to the BA, the field makes the system less dispersive: β_2 shifts from ≈ 0.2 – 0.4 up to 0.90 . So this behaviour corroborates the existence of a strong coupling between these modes.

In order to carry out a quantitative study of the data concerning the relaxation times of BA and DBA92 we have followed a similar analysis to that used by Grossmann *et al* [14] in the study of $\text{AgNa}(\text{NO}_2)_2$.

In the paraelectric phase (HT mode) the activation energy (ΔU) of the potential barriers in an order–disorder material is given by:

$$\tau_1 = \frac{T}{C} \Delta\epsilon_1 \Gamma^{-1} \exp\left(\frac{\Delta U}{kT}\right)$$

where C is the Curie–Weiss constant, Γ a characteristic frequency and $\Delta\epsilon_1$ the dielectric amplitude [14]. In figure 7, $\ln(C/\tau_1)$ as a function of the temperature is displayed for BA and DBA92 at zero field and under d.c. fields. For BA at zero field we have found

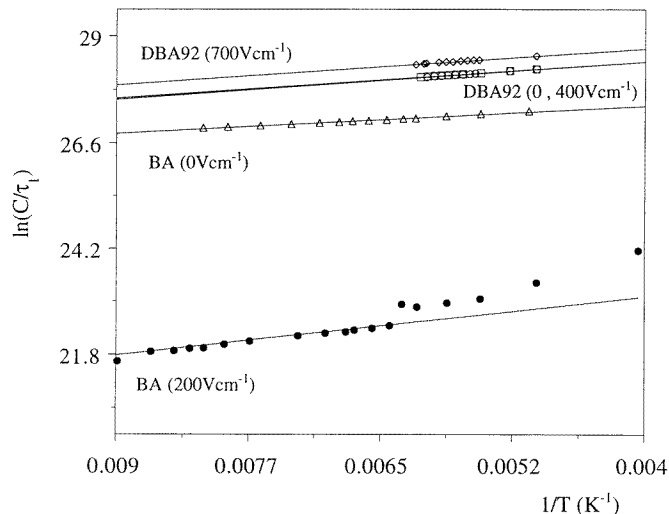


Figure 7. Logarithm of C/τ_1 versus the inverse of temperature.

$\Delta U \approx 0.010$ eV ($T \approx 120$ K); for BA ($E = 200$ V cm $^{-1}$), $\Delta U \approx 0.023$ eV ($T \approx 300$ K) and for DBA92 ($E = 0$, $E \neq 0$) $\Delta U \approx 0.015$ eV ($T \approx 168$ K).

For zero field the values found for BA and DBA92 are in good agreement with the critical temperatures of a order–disorder phase transition. In DBA92 the result is independent of the d.c. applied electric field. The electric field upshifts in an very explicit way ΔU for BA which means the existence of a coupling of HT and LT modes of BA under a d.c. field.

The coexistence of antiferro- and ferroelectric interactions at low temperatures in BA and DBA92 yields a behaviour that bears some resemblance to the properties of systems with competitive interactions like orientational glasses. It is remarkable that such a behaviour was found in a pure system. In fact, it is well known that some solid solutions of antiferro- and ferroelectric compounds behave like orientational glasses. Illustrations of this situation occur in the KDP family [15]. Recently, it was reported that a freezing transition at a finite temperature was found in the mixed compound of the antiferroelectric deuterated betaine phosphate and the ferroelectric deuterated betaine phosphite [16]. The study of the relaxational behaviour of a mixed compound of betaine phosphate and betaine phosphite provided also evidence for a transition into an orientational glass state [17].

4. Conclusions

This work shows that the main contribution to the dielectric constant in BA and DBA92 arises from low-frequency relaxation modes. The broad anomaly of dielectric constant in BA at 110–120 K is due to para–antiferroelectric and antiferro–ferroelectric transitions occurring at very close temperatures, shifted by 4–5 K. The strong distortions of hysteresis loops in BA close below $T_{C_2}^H$ are understood on the basis of the analysis done in this work. The main contribution to $\varepsilon'(T)$ is due to a ferroelectric mode in BA and to an antiferroelectric mode in DBA92. The results obtained lead us to associate mainly the protons (deuterons) to the antiferroelectric transition and the AsO_4^{3-} anion and betaine molecules to the ferroelectric transition. In the protonated system a coupling of the relaxation modes is enhanced by a

d.c. field, but in the deuterated one there is no explicit coupling of the modes. In DBA92 the relaxation times are increased and the dielectric amplitudes are decreased in comparison with BA.

Acknowledgments

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