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Dielectric and structural properties of iron- and sodium-fumarates

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Abstract

The behaviour of dielectric parameters such as the relative dielectric constant (ε'), the relative loss factor (ε'') and the ac conductivity of well known pharmaceutical materials Fe(II)-fumarate and Na-fumarate were studied as a function of temperature (in the range from 303 K to 483 K) and frequency (in the range from 0.1 Hz to 100 kHz). The values of the conductivity are in the range of $10^{-5}\,\Omega^{-1}\mathrm{m}^{-1}$ to $10^{-9}\,\Omega^{-1}\mathrm{m}^{-1}$ for Fe(II)-fumarate and $10^{-6}\,\Omega^{-1}\mathrm{m}^{-1}$ to $10^{-11}\,\Omega^{-1}\mathrm{m}^{-1}$ for Na-fumarate. The conductivity of both materials increases with the increase in temperature and frequency. It was found that both ε' and ε'' decrease with increasing frequency and increase with increasing temperature for both materials. The highest changes are in the low frequency range. The obtained values of the dielectric parameters and conductivity suggest that these materials are dielectric with similar structure, most probably polymeric, with the mechanism of ionic conductivity.

Key words: Fumaric acid salts, electrical characterization, powder diffraction, dielectric phenomena

1. Introduction

Iron(II)-fumarate and Na-fumarate are well known pharmacological materials. Fumaric acid is *trans*-1,2-ethylendicarboxylic acid ($C_4H_4O_4$) with the structural formula shown in Fig. 1a. Ferofumarate (ferrous fumarate or iron(II) fumarate) is the salt of fumaric acid and bivalent iron in the form of fine redish-brown powder with the structural formula shown in Fig. 1b [1]. Its medical application is based on the following facts. It is assumed that about 20-30 % of the world population suffers from hyposideremy (lack of iron and sideropenic anaemia), so that the prevention and therapy of such conditions are permanently existing problems in human medicine [2]. In order to overcome this problem, a great number of pharmaceutical materials based on ferrous or ferric ion are used. Oral therapy is based on the medicaments containing salts of bivalent iron such as ferrosulphate, ferrofumarate, ferrogluconate, etc. with ferrofumarate most broadly used. This fact is due

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to its good properties such as good absorption in the organism and low toxicity. Good absorptiveness in the organism origins from fumaric acids which is an intermedier in the cycle of tricarbon acids and as such abundant in living organisms (Crebbs cycle or lemon acid cycle) [1,2]. Sodium-fumarate is one of the initial compounds in ferrous fumarate synthesis, and it is also a pharmaceutically active compound (food additive, acidity regulator) [3].

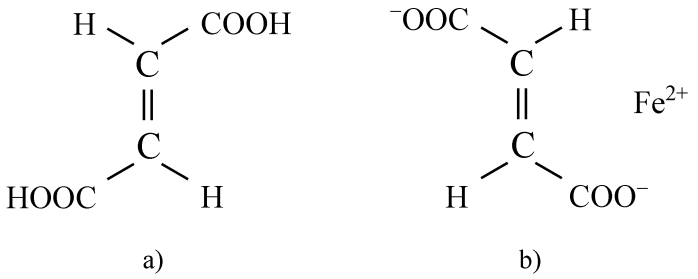

Figure 1. a) Fumaric acid. b) Ferrous fumarate.

The characterization of the material was previously performed (IR-spectroscopy, DSC and the measurement of the magnetic susceptibility) in order to identify the structure. For ferrous fumarate, the results of magnetic measurements indicate that Fe(II) ion within the studied complex appears in the low-spin state, with two unpaired electrons, pointing towards a coordination polyhedron in the shape of an elongated octahedron [4]. The analysis of IR-spectra confirmed that the carboxylic ions of fumaric acid are bonded asymmetrically bidentatly to Fe(II) ions (Fig. 2) [5-8].

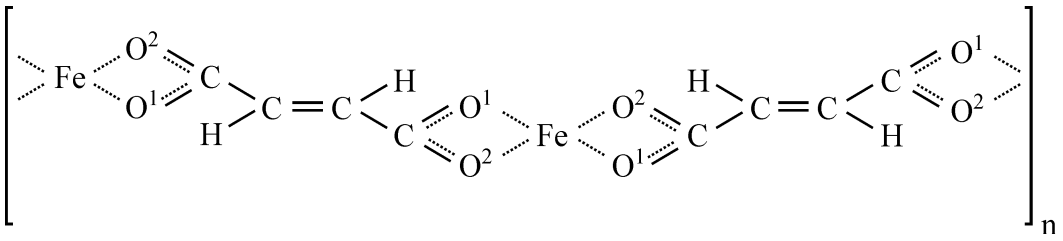

Figure 2. Presumed structural formula of Fe(II)-fumarate.

A similar environment of the Na ion in Na-fumarate was confirmed in the solved crystal structure (Fig. 3) [9]. One can conclude that iron and sodium ions are surrounded by the oxygen atoms forming a coordination polihedron in the shape of an elongated octahedron. In the crystalline state, iron(II)-fumarate forms most probably a macromolecular chain (Fig. 4) (software ChemDraw 9.0, 2004). The remaining two axially coordinated oxygen atoms probably belong to the molecules of the crystalline water.

The analysis of the dielectric characteristics and the conductivity of these materials was performed in order to complete the image of the crystal structure and properties of chemical bonds of these compounds, all with the purpose of a better interpretation of the pharmacological activity in the living organism at the molecular level, as well as defining the further application of the given materials. Measurements of the dielectric

properties of materials are helpful in understanding the present types of polarization. The *ac* conductivity measurements have been used to clarify the conduction process in these materials [10].

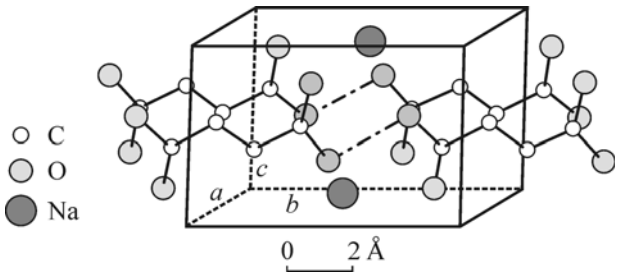

Figure 3. Crystal packing of Na-fumarate.

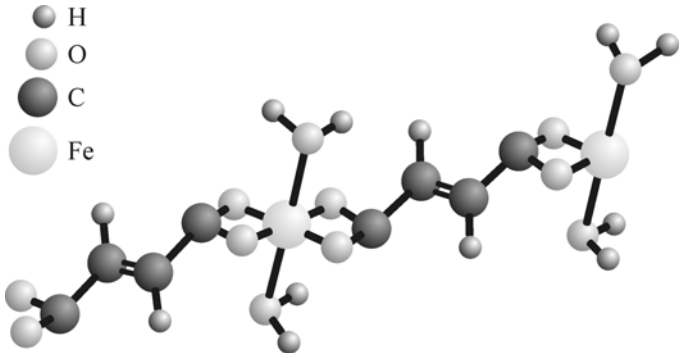

Figure 4. Modelling structure of Fe(II)-fumarate with two water molecules.

Under the presence of electromagnetic field, various materials interact and respond differently to the alternating electric field. The ability of a material to interact with the electromagnetic field depends strongly on the microstructure and the type of bonding in the material.

The relative dielectric constant (ε') determines the maximal energy that can be stored in the material. The relative loss factor (ε'') describes the absorption of the electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. The loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) determines how well a material can absorb the electromagnetic field [11].

2. Material and methods

2.1. Materials

The samples of the polycrystalline complex of Fe(II)-fumarate were synthesized in the reaction of Na-fumarate (Merck) and ferrous sulphate. Na-fumarate was previously obtained by the neutralization of the fumaric acid (Carlo Erba-Milano, $> 99,5\%$) with the corresponding amount of sodium hydroxide and crystallization from water. Since it

is known that Fe(II) ion oxidizes at the atmospheric pressure rather easily to Fe(III) ion, which is additionally intensified by the heating, the synthesis was performed under the lowered pressure in order to minimize the oxidation process. This approach minimizes the contents of Fe(III) ions in the final synthesized product of ferrous fumarate. Fe(III) ion is not welcome in any oral drug due to its toxicity [12,13].

2.2. Experimental procedures

The crystal structures of the new synthesized powder samples of Fe(II)-fumarate as well as of the initial substance Na-fumarate were checked by XRD analysis. The X-ray diffraction patterns of the substances were measured on a Philips 1050 automatic powder diffractometer, using Ni-filtered CuK_α radiation in the range from 5 to 65 ^{o}, with a step of 0.05 ^{o} and the exposition time of 5 s.

Samples for the dielectric measurements were prepared in the form of compressed pellets of 10 mm in diameter and 1.34 mm thickness for Fe(II)-fumarate and 1.6 mm for Na-fumarate. The instrument used for all measurements of dielectric parameters and specific conductivity was a fully automatized dielectric spectrometer DEA 2970 (DuPont Instruments, USA). The measurements were performed in the frequency range from 0.1 Hz to 100 kHz, starting from the room temperature up to below the melting temperature (determined by the DSC analysis).

3. Results and Discussion

Results of XRD analysis are shown in Fig. 5 and Fig. 6. The XRD analysis confirmed that the synthesized samples were actually Fe(II)- and Na-fumarate (ICSD - Inorganic Crystal Structure Database, PCPDFWIN Version 2.4, PDF Number 23-1730 and 35-1796). Typical results of the temperature dependence of the relative dielectric constant (ε'), the relative loss factor (ε''), and of the *ac* conductivity, at some representative fixed frequencies for Fe(II)-fumarate are shown in Figs. 7, 9 and 11, and for Na-fumarate in Figs. 8, 10 and 12.

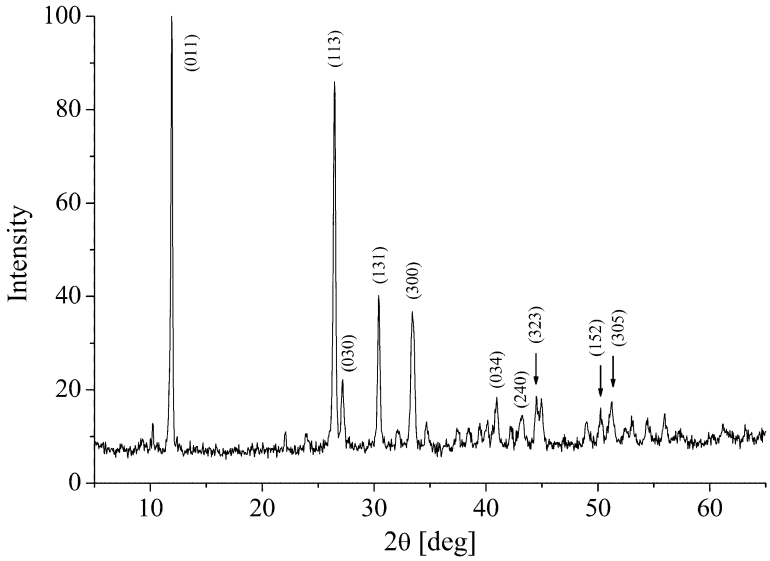

Figure 5. X-ray diffractogram of Fe(II)-fumarate.

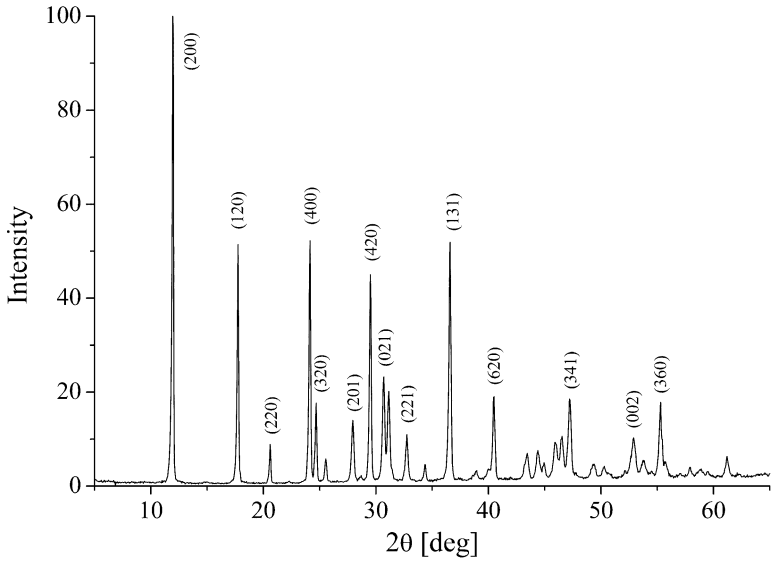

Figure 6. X-ray diffractogram of Na-fumarate.

The inserted plots (Figs. 7-12) show the results of the measurements of ε', ε'' and σ_{ac} as a function of frequency at some representative fixed temperature. Both samples exhibited dielectric dispersion. The values of ε' and ε'' for Fe(II)-fumarate and Na-fumarate decreased with increasing frequency at a fixed temperature. The value of ε' was high at low frequencies. This type of behaviour has been observed for many materials. The observed behaviour has been explained by the phenomenon of dipole relaxation wherein at low frequencies the dipoles are able to follow the frequencies of applied field, while at higher frequencies dipoles are not able to follow the frequencies of the applied field [14].

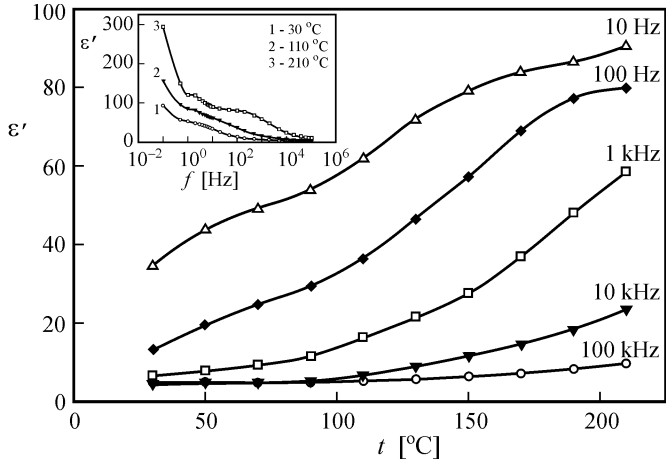

Figure 7. Temperature dependence of ε' for Fe(II)-fumarate;
Inset: the frequency dependence of ε'.

The decrease of the relative dielectric constant with the frequency can be attributed to the fact that at low frequencies ε' for polar material is due to the contribution of multicomponents of polarizability, deformational (electronic, ionic) and relaxational (orientational

and interfacial). When the frequency is increased, the orientational polarization decreases since it takes more time to follow then the electronic and ionic polarization. This decreases the value of the dielectric constant with the frequency, reaching a constant value at a high frequency, due to interfacial polarization [10].

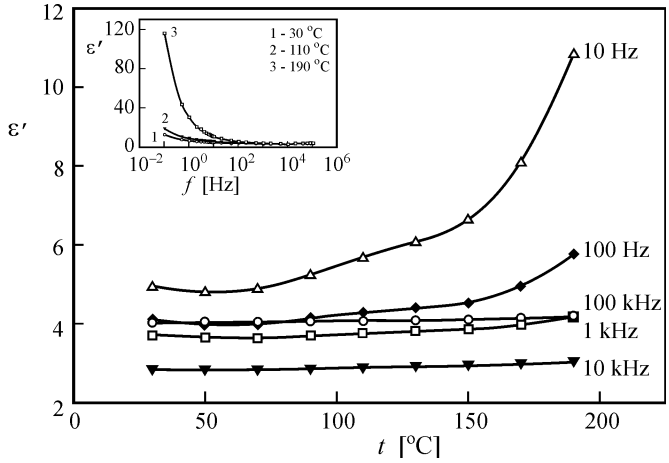

Figure 8. Temperature dependence of ε' for Na-fumarate;
Inset: the frequency dependence of ε'.

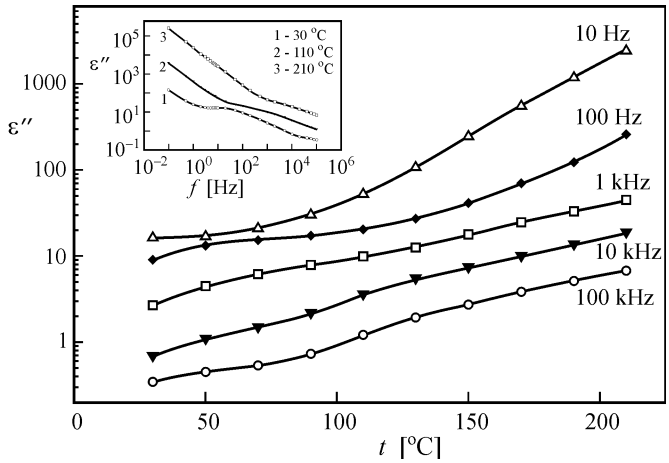

Figure 9. Temperature dependence of ε'' for Fe(II)-fumarate;
Inset: the frequency dependence of ε''.

For Na-fumarate one observes that the frequency dependence of ε' and specific conductivity has a sudden drop at the frequency of 20 kHz. This effect is substantially more expressed at lower temperatures (Figs. 8 and 10). For the temperature dependence of ε' and specific conductivity one can also observe a minimum at the temperature of 70^{o}C, while the frequency curves have a minimum between 10 kHz and 20 kHz.

The sudden drop of the value of dielectric loss ε' indicates an increased contribution of the relaxational (orientational) polarization at the observed frequency, which can be related to the structure of Na-fumarate in the solid state. Suh a frquency, close to 43 kHz,

was found in the study of the dependence of dynamics of the polymeric fumarate chain on the temperature and frequency [15], and it is attributed to the chain reorientation. The absence of this phenomenon for Fe(II)-fumarate in the measured frequency range is a consequence of a stronger coordination bonding of Fe(II) ion.

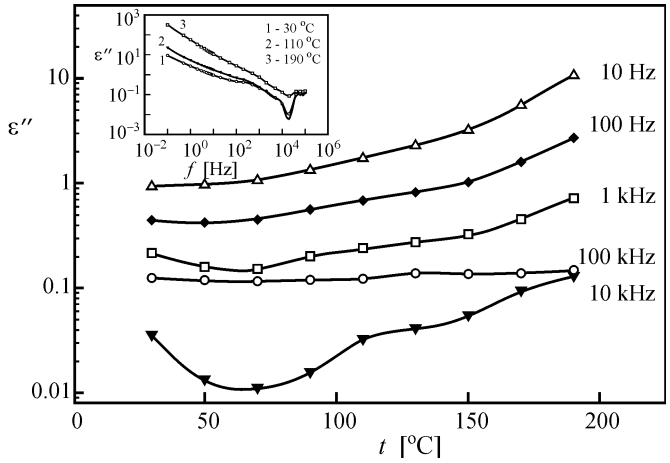

Figure 10. Temperature dependence of ε'' for Na-fumarate;
Inset: the frequency dependence of ε''.

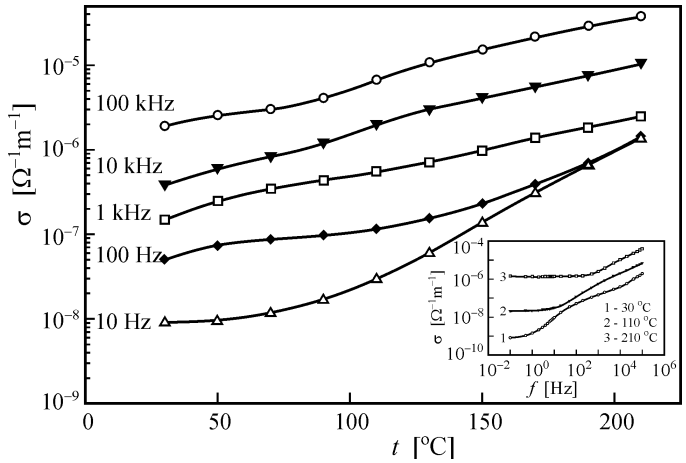

Figure 11. Temperature dependence of σ for Fe(II)-fumarate;
Inset: the frequency dependence of σ.

The dielectric parameters (ε' and ε'') and conductivity for both materials exhibited an increase with increasing temperature. The increase of (ε') with temperature can be attributed to the fact that the orientation polarization is related to the thermal motion of molecules. Dipoles cannot orient themselves at low temperatures. When the temperature is increased, the orientation of dipoles is facilitated, and this increases the value of the orientation polarization and of the relative dielectric constant with increasing temperature.

The conductivity measured for both of these materials increases with increasing temperature and with increasing frequency, as it was expected. On the plots one can observe

that σ_{ac} increases with temperature, following approximately an exponential law. This is especially expressed in the low-frequency region. If the sample consists of macromolecular chains, then the chain itself does not participate in the charge transfer, but its mobility can enhance or decrease the free ion mobility [16]. The mobility of a macromolecule increases with the temperature rise and the specific conductivity rises following an exponential law. In this way, we have obtained an additional result, the confirmation of the assumption about the polymeric structure of these materials. The values of the conductivity are in the range of $10^{-5}\,\Omega^{-1}\mathrm{m}^{-1}$ to $10^{-9}\,\Omega^{-1}\mathrm{m}^{-1}$ for Fe(II)-fumarate and $10^{-6}\,\Omega^{-1}\mathrm{m}^{-1}$ to $10^{-11}\,\Omega^{-1}\mathrm{m}^{-1}$ for sodium-fumarate.

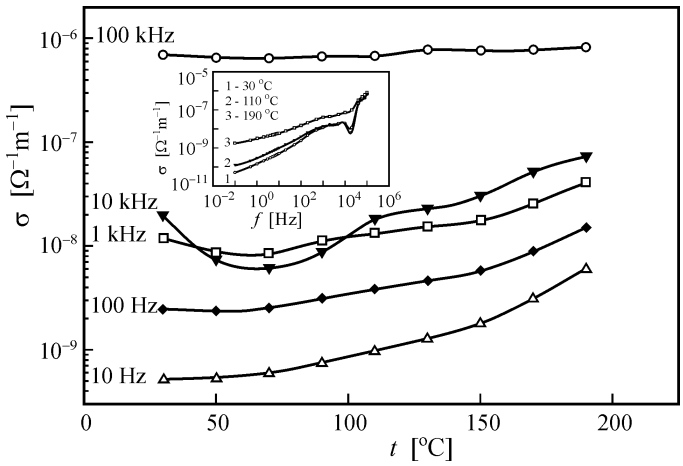

Figure 12. Temperature dependence of σ for Na-fumarate; Inset: the frequency dependence of σ.

4. Conclusion

A comparison of the results of the dielectric and conductivity measurements for Fe(II)- and Na-fumarate showed a more expressed frequency and temperature dependence of ε', ε'' and σ_{ac} for Fe(II)- than for Na-fumarate. Also, the values of the relative dielectric constant, relative loss factor, and *ac* conductivity are higher for the Fe(II)-fumarate than for Na-fumarate.

The obtained similar overall frequency dependence of the dielectric parameters and conductivity suggests similar structure of the two materials. Although the crystal structure of Fe(II)-fumarate has not been solved yet, based on the similarities in the dielectric behaviour of Fe(II)- and Na-fumarate at low frequencies, it may be concluded that these materials are dielectrics with the mechanism of ionic conductivity, and that they posses similar packing in the crystal lattice, i.e. that they form polymer chains.

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