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Electrophysical Properties of Natural Armenian and Syrian Zeolites

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Abstract. Using an experimental arrangement, designed and constructed locally, the electric permittivity ε=ε'-iε'', alternative current (a.c.) conductivity σ_{ac} and direct current (dc) conductivity σ_{dc} of natural Syrian and Armenian zeolites are investigated in order to understand the mechanism of electrical conductivity in these materials. We also study the frequency dependence of angle tangents (tanδ=ε''/ε') of dielectric losses of studied zeolitic samples. The mentioned measuring arrangement has a configuration of an electrical bridge. The obtained data show that the dielectric constant ε' and dielectric loss ε'' of all the studied samples decrease when increasing the frequency of applied electrical field from 200 *Hz* to 1 *MHz*. Moreover, it was found, for all the studied samples, that the ac conductivity σ_{ac} increases with increasing the frequency of the applied field. The ratio of the increase depends itself on the applied frequency. The influence of the sample's water content on its electrical conductivity and dielectric parameters is studied in details.

Keywords: natural zeolite, dielectric properties, electrical conductivity

1. Introduction

Zeolites are natural minerals that are mined in many parts of the world or synthesized by man. They are characterized by a microporous, crystalline structure consisting of a three-dimensional framework of SiO_4 tetrahedra where all four-corner oxygen ions of each tetrahedra are shared with adjacent tetrahedra. Some of the quadrivalent silicon is replaced by trivalent aluminum, giving rise to a deficiency in positive charge. This charge deficiency is balanced by the presence of mono and divalent cations located in the pores. These cations are highly mobile and can be exchanged for other cationic species. The Si/Al ratio of natural zeolite is in the range of [1-6]. Loosely bound water is also present in the pores of natural zeolites and range from $10\text{-}20 wt.\%$ of the dehydrated phase. Zeolites have void spaces (cavities or channels) that can host cations, water or other molecules. Cavities in zeolites enable them to screen molecules and sieve cations. Cation exchange capacity is primarily a function of the degree of Al substitution for Si in the structure: the greater the substitution, the higher is the deficiency of the positive charge and the greater is the number of alkali cations needed to achieve electrical neutrality. However, cation exchange capacity also depends on other factors, such as exposure of the zeolite to cations that are easily trapped in the structure but which can not be removed easily.

The size of the cations also has an effect on cation exchange capacity. The large cavities and entry channel of zeolites are generally filled with water molecules that form hydration spheres around the exchangeable cations.

The physical and chemical properties of natural zeolites in that they can capture and immobilize ammonium ions, water, and certain cations has resulted in numerous investigations into developing agricultural and/or horticultural applications for them. In fact, the following uses of zeolites have been investigated: holding and slow releasing valuable nutrients to plants, mainly ammonium; uses in conjunction with nitrogen $\left(NH_4^+\right)$, potassium $\left(K^+\right)$, magnesium $\left(Mg^{2+}\right)$, calcium $\left(Ca^{2+}\right)$ and trace elements; promoting better plant growth by improving the value of fertilizer; prevention of plant burning from over-use of fertilizers by trapping and slowly releasing valuable nutrients; improving the cation exchange capacity of soil resulting in less fertilizer requirements; and improving the water retention of soil. However, U.S. Pat. No. 5,900,387 reports experiments on clinoptilolite which has been reported as having a high affinity and selectivity for $\left(NH_4^+\right)$. Moreover, nowadays an extensive attention is paid on Jordanite. The zeolitic component of Jordanite is primarily phillipsite, but a minor amount of chabazite may also be present. In this embodiment, the phillipsite may be present in amounts ranging from about 10 to about $90 wt.\%$ and the chabazite in amounts ranging from about 1 to about $20 wt.\%$.

The measurement of the specific electrical conductivity σ of zeolites is one of the most attractive procedures to determine their properties [1-10]. Usually, the measurement of σ of zeolitic samples takes place at the alternative current (ac) condition (variable electrical field) in order to avoid various effects such as polarization, relaxation processes, electrolyze, etc [1-8]. It was found that σ is highly dependent on the applied frequency of the electrical field. Therefore, it is recommended that one measures σ within a wide range of frequencies in order to have an idea, sufficiently correct, about the mechanism of electrical conductivity in the zeolites [2]. Moreover, the measurement of σ at constant electrical field conditions (direct current (dc) conditions) somehow gives an overestimate. The results of the measurements, obtained using these two methods, could be integrated in order to give a real picture of the electrical conductivity [3-7].

In addition to the above mentioned properties, it is well known that zeolites have a large forbidden energy gap $(\sim 7eV)$ [8], and that their electrical conductivity, in value, is near to that of bad dielectrics. On the other hand, the characteristic behavior of the electrical conductivity of dielectrics is such that when applying a constant electrical field on a dielectric sample, the intensity of the current, passed through the sample, decreases with time [11-13]. In fact, at the start, bias current with quickly decreasing intensity passes through the circuit, then, this current disappears at a time equal to the order of the RC system (generator-sample) constant time, which is very small (less than 1 s). However, the current can continue its decrease for some minutes, voire some hours in cases of samples with big dimensions. The time required for current stabilization could be decreased by adjusting the dimensions of the sample.

The component of slow changing current is due to the redistribution of free charges in the volume of the dielectric. This component is known as the absorption current, and it is caused by the absorption of free current carriers in the volume of the dielectric. Part of these carriers, during their movement, will meet defects-traps of crystalline lattice causing them to be trapped and stopped. With time, the traps could be filled by current carriers, then, the absorption current disappears. The rest of the current does not depend on time and it is due to the charge carriers which pass from one side of the sample to the other (i.e. from one electrode to another). Thus, the absorption current leads to the accumulation of current carriers in separate parts of the dielectric, for example in the destroyed parts of the crystalline lattice, or at the grain boundaries, or/and in other types of inhomogeneities. As a result of the space charge appearance, the distribution of the electrical field becomes inhomogeneous. The accumulation of space charge in the dielectric leads to an undesired phenomenon in that the charged capacitor does not discharge totally after wiring its plates (short circuit). This effect is characterized by the coefficient of absorption which is determined as the ratio of the residual to the initial voltage.

When measuring the specific electrical conductivity, the absorption current could be eliminated by applying temporarily a constant voltage on the sample electrodes. All what we mentioned of phenomena do happen in the zeolitic samples and the arguments above do apply. Thus, the measurement of the specific electrical conductivity of zeolites is completed, in fact, by measuring the current which passes through the samples, i.e. the steady leakage current [11].

The investigation of dielectric characteristics of zeolite during the process of hydration and dehydration gives important information about its sorption capacity and catalytic activity [2, 3, 5, 9, 14-16]. The measurement of electric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ and a.c. conductivity σ_{ac} of zeolites, having ionic or mixed ionic/electronic conductivity, is used generally to investigate the zeolite sorption properties of water vapor, since the absorbed water molecules in zeolites play a basic role in electrical behaviors [2] of these materials at room temperature. The aim of this work is to shed a light on these questions regarding Syrian and Armenian natural zeolites which contain clinoptilolite (the Armenian one) and the main components of jordanite (the Syrian ones).

2. Materials and techniques

In this work, the investigated samples have been prepared from grounded Syrian (S) and Armenian (A) natural zeolites. The Armenian zeolite, denoted by $A12$, contains up to 85% of clinoptilolite with a ratio of Si/Al equal to 9 and amorphous SiO_2 less than 3%. The Syrian zeolitic tuff contains mainly about 50% of three types of zeolite (analcime, phillipsite and chabazite). The chemical composition of the studied samples is given in the Table 1. The samples were ground and pressed in pellets of $2-3mm$ in thickness at about $1470\, N/cm^2$ of pressure. From these pellets, samples of $30mm^2$ in surface were taken mechanically. The two plate surfaces of each sample were coated using silver contacts. After that, samples were thermally treated at temperature 120^0C for two hours followed by thermal treatment at 220^0C for two extra hours. This treatment was performed in order to obtain reliable good silver contacts.

The measurement of electric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ of the studied samples was carried out using a special and nonstandard arrangement which is designed and constructed, locally, for this purpose. The mentioned arrangement allows to measure electric permittivity corresponding to electrical field with frequencies from $200Hz$ to $1MHz$ and with sinusoid applied voltage amplitude of $25mV$ at the contacts of the sample. This measuring arrangement has a configuration of an electrical bridge. In addition to the alternative electric field a direct current (d.c.) electric field could be applied at the studied sample. The dc voltage could vary from 0 to $\pm 20V$. The scheme of the arrangement is shown in Figure 1. The unbalance signal of the bridge is applied, after magnification, to the inputs of lock-in detectors while the conductivity and capacitance of the samples were measured at the output of these detectors. The capacitance was measured using the reading of calibrating condenser (Cc) at the zero-th indication of lock-in detector regarding C. In this arrangement three measuring transformers were used over the frequency interval ranging from $200Hz$ to $1MHz$.

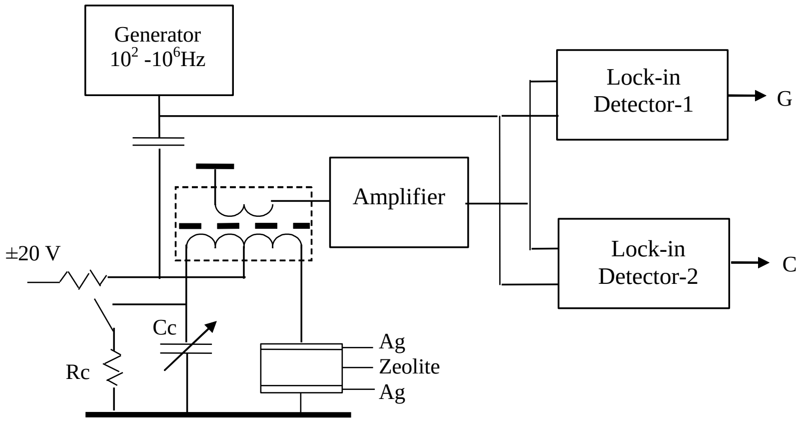

Fig.1: Scheme of the measuring arrangement. Rc stands for calibrating resistor, Cc stands for calibrating condenser.

The accuracy of the measurement of the dielectric parameters is about 7%. Here it should be noted that the measurement of dielectric parameters of studied samples was carried out in the air at room temperature. The relative humidity of the ambiance during the experiments was varied from 50% to 60%. So, at these conditions the absorbed, by zeolitic samples, water content makes $\sim 9\%$ of the sample mass.

In order to measure the dc conductivity σ_{dc}, a universal voltmeter $V7-16$ is used with an input resistance equal to 10 MΩ (for dc), in addition to a nano-voltmeter $P341$ having an input resistance of 100 Ω approximately and minimal scaling of $0.005nA$ (for dc). Since the input resistance of the voltmeter is less than the resistance of the sample itself (or near to it), the voltmeter is not connected to the sample directly. As usually done, in the case of samples with low resistance, the voltmeter should be connected in parallel to the sample and to the Amber meter simultaneously in order to avoid current pass through the voltmeter. The mentioned scheme is well described in the literature. In fact, the voltmeter is connected to one side of the sample while the other side is connected to the Amber meter.

3. Results and discussion

3.1 A.c. characteristics

The electric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ and a.c. conductivity σ_{ac} of zeolite present important information for understanding the mechanism of electrical conductivity in these materials. Figures 2 and 3 show the frequency dependence of dielectric constant ε' and dielectric loss ε'' of the studied samples respectively. It is seen from these figures that the behavior of these two parameters is qualitatively similar regarding their dependence on the frequency of the measured electrical field. The obtained data show that the dielectric constant ε' and the dielectric loss ε'' of all studied samples decrease when we increase the frequency of applied electrical field from $200Hz$ to $1MHz$. This property is characteristic for natural zeolites and synthetic ones of US-HY type [5]. Another characteristic property is that dielectric parameters have relatively high values and they may change in a large interval of frequency.

Moreover, the dielectric response of zeolites is highly sensitive to the water content of samples. It is supposed that electrical dipoles, which appear in the sample as a result of formation of H^+ and OH^- forms of adsorbed water in the crystalline cells, are mainly responsible for the dielectric response. In order to somehow verify this assumption, the clinoptilolite sample was thermally treated at temperature of 800^0C for $100\min$. As a result of this treatment the crystalline structure of the studied sample disappeared totally according to X-ray diffractometric (XRD) investigation. When we measured the dielectric constant ε' and dielectric loss ε'' of the studied sample before and after the thermal treatment we found that the values of these two parameters largely decreased after treatment. The water content of the studied sample after treatment was equal to half its value before treatment. This experimental fact could be taken as an indication of the validity of the given assumption.

The frequency dependence, of angle tangents $\left(\tan\delta = \varepsilon''/\varepsilon'\right)$ of dielectric losses of the studied zeolitic samples, is given in Fig. 4. It is seen from Fig.4 that these curves have some special characteristic features for all the studied samples. One of these features is that $\tan\delta = \varepsilon''/\varepsilon'$ decreases when increasing the frequency of the applied electrical field. At frequencies near to 1MHz, the values of $\tan\delta = \varepsilon''/\varepsilon'$ for all the studied samples are very near to each other. The second feature is that $\tan\delta = \varepsilon''/\varepsilon'$ for all studied samples differs significantly from one sample to another in both its value and the character of the low frequency dependence of the applied electrical field. Some of these figures have a wide maximum while others tend to show this wide maximum. The appearance of wide maximum of $\tan\delta = \varepsilon''/\varepsilon'$ at low frequency of the applied electrical field is an indication to the fact that the studied zeolitic samples are polar materials. Indeed, the molecules of these materials contain groups having constant dipole moment [9]. In such materials a relaxation polarization and losses are developed. When the frequency of the applied field increases the values of ε' decrease while the values of ε'' pass through a maximum. However, as it is seen from Fig. 2, the maximum of ε'' is not observed. This is probably due to the relatively high value of the initial frequency of the applied field. Thus, it is probable to observe this maximum at frequency lower than $200Hz$.

Here it should be noted that $\tan\delta$ is a parameter which does not depend on the density of electrical dipole moments of the studied materials but it characterizes these dipoles. In fact, $\tan\delta$ constitutes a source of information for the structural changes in these dipoles and their ambiance surrounding. From this point of view, the significantly observed differences of $\tan\delta$ parameter (see Fig. 4) allow us to assume that the structure of the crystalline cells of the studied samples is quite different. Moreover, this can be due, in particular, to the availability of different defects and impurities in the crystalline cells.

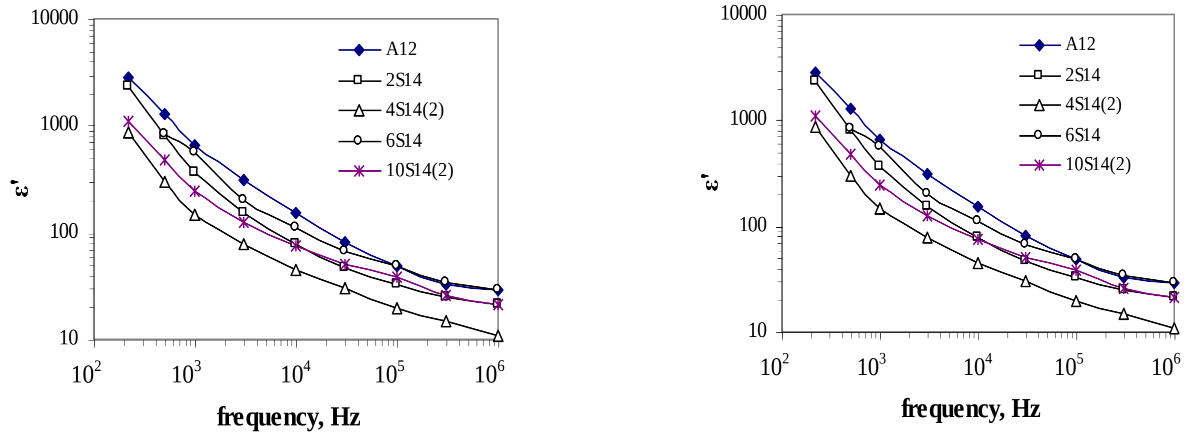

Fig. 2: The frequency dependence of dielectric constant ε' of the studied samples.

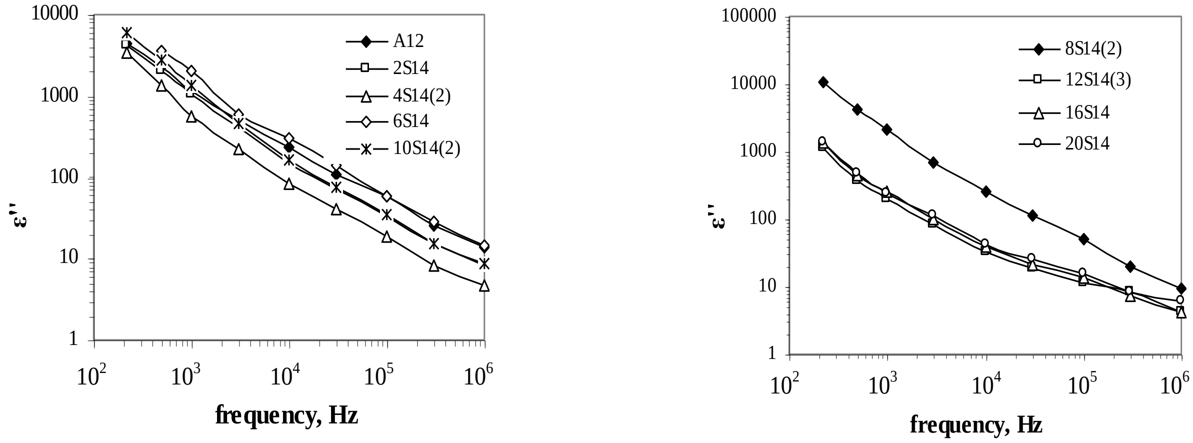

Fig. 3: The frequency dependence of dielectric loss ε'' of the studied samples

The frequency dependence of alternative current (ac) conductivity σ_{ac} of the studied samples is given on Fig. 5. The ac conductivity σ_{ac} could be calculated using the well-known formula $\sigma_{ac}=\varepsilon_0\omega\varepsilon''=2\pi f\varepsilon_0\varepsilon''$, where ε_0 is the vacuum permittivity, ω the angular frequency [7]. For all the studied samples it was found that ac conductivity σ_{ac} gets larger when the frequency of the applied field increases. The ratio of the increments depends itself on the applied frequency. At very low frequencies it is observed a region where ac conductivity σ_{ac} remains practically constant, but at higher frequencies, it is observed a monotonous increasing of ac conductivity σ_{ac} with frequency. Similar results were found for US-HY type zeolite [5] and for synthetic dehydrated zeolites NaY and HY [19, 20]. In addition to the above mentioned experimental arrangement, a standard impedance meter was used to measure the electrical conductance and capacitance using special measuring cell. Samples were ground and then pressed in pellets of $2-3mm$ in thickness and of $25mm$ in diameter at about $1470\,N/cm^2$ of pressure. Al electrodes were vacuum deposited on both sides of the samples. The prepared electrodes were circular in shape with diameter of about $20mm$. After that, the samples were thermally treated at temperature of 120^0C for two hours followed by additional two hours of thermal treatment at 220^0C. Data were collected in voltage drive mode employing a linear sweep over the frequency range $100kHz$ to $13MHz$. The amplitude of the measure ac-voltage signal was $1V$. PC interface was used for data acquisition where connection to the frequency response analyzer was performed by screened coaxial cable of $1m$ in length. The obtained data agree with the mentioned above results.

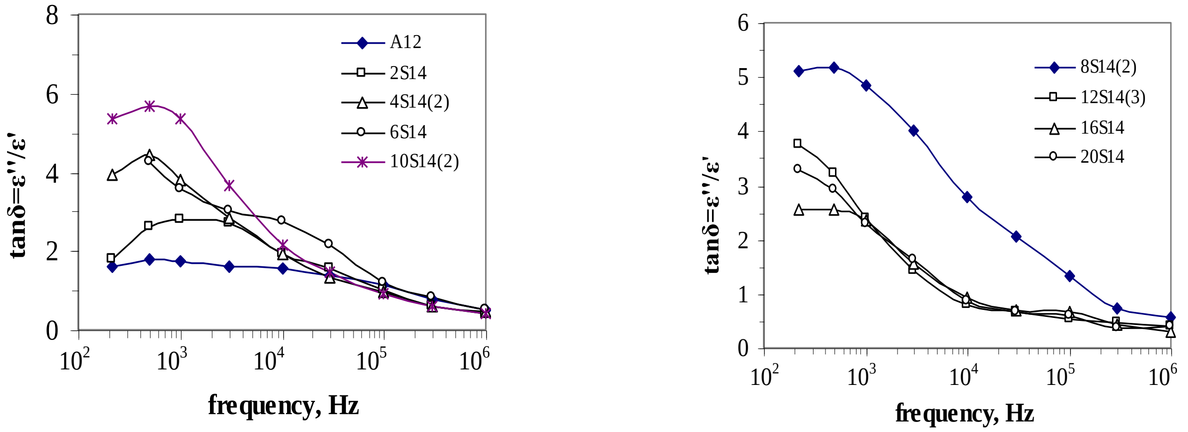

Figure 4: Frequency dependence of angle tangents of dielectric losses of studied zeolitic samples.

The dependence of dielectric parameters of the studied zeolitic samples on the absorbed water content was measured at ambient temperature $(T = 294K)$ and measuring frequency of electrical field equals to $f = 1kHz$. The results are presented in Figure (6-a) where $\Delta m\% = \frac{(m-m_0)}{m_0}\cdot 100\%$, $m_0 -$ is the samples mass at full dehydrated state and $m -$ is the samples mass at hydration process.

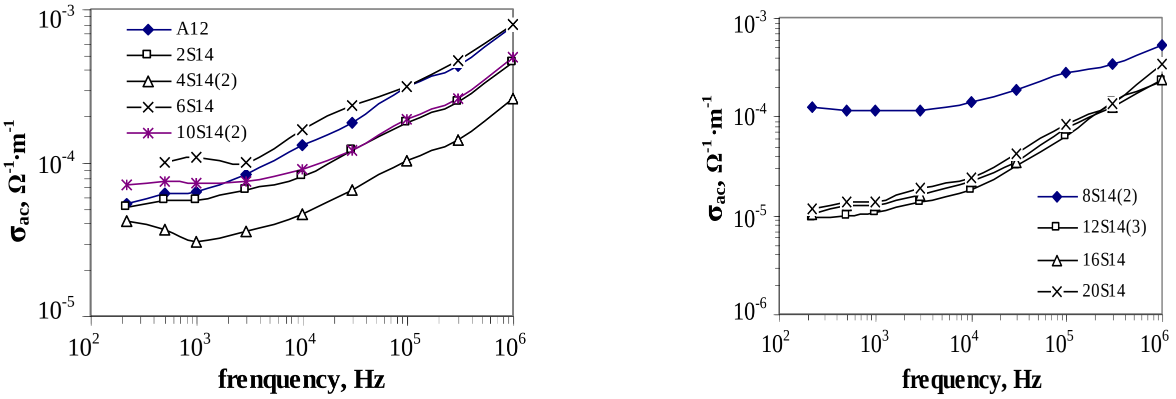

Figure 5: Frequency dependence of ac conductivity of the studied samples.

It is seen from these results that there is a strong dependence of dielectric parameters ε' and ε'' on the absorbed water content and these parameters reach a very big value of order of 10^4. Basing on these data one can conclude that in the process of hydration the dielectric response of the studied zeolites has a specific character and it is not due to dipole momentum of water molecules absorbed by the samples (for water $\varepsilon' = 81$). This should be due to other phenomenon. Moreover, the dependence of angle tangents of dielectric losses of studied zeolitic samples (see Fig. (6-b)) on the water content of zeolite is of complex character.

The dependence of dielectric parameters on thermal treatment at different increasing temperature rates is given in Figs. (7) and (8). It is seen from these figures that the dielectric parameters ε' and ε'' of zeolitic samples decrease with increasing temperature at a very low rate. A large maximum of ε' and ε'' is observed with increasing temperature rate. In our opinion, we deal in this case with two different processes which take place simultaneously during the thermal treatment of the zeolitic samples.

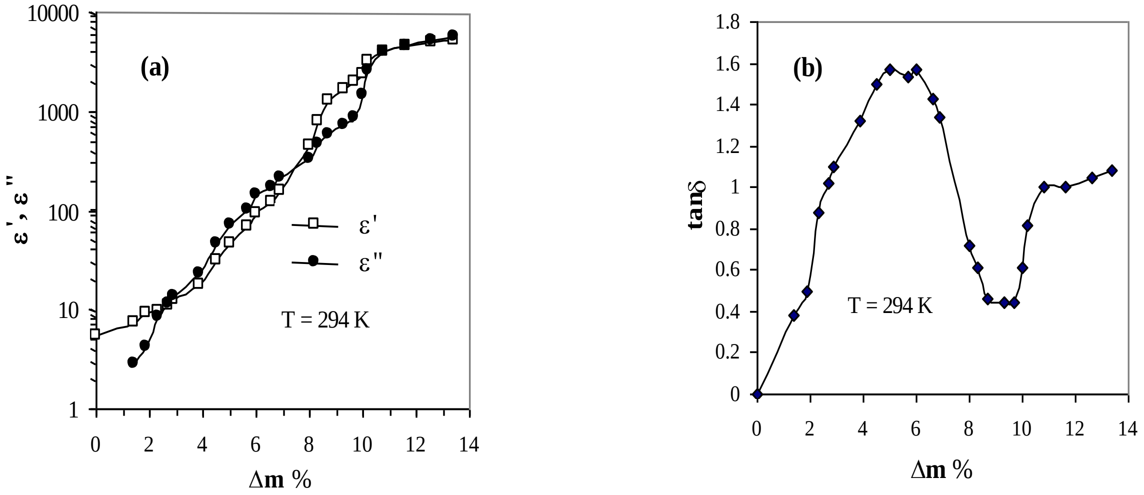

Fig.6. The dependence of dielectric permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ (a) and dielectric losses factor $\tan\delta = \varepsilon''/\varepsilon'$ (b) of Armenian natural zeolite (clinoptiloite 85%), versus absorbed water mass:

First, with sample thermal treatment the process of decreasing absorbed water content starts. So, the values of ε' and ε'' will decrease (see Fig. 6a).Second, at constant value of absorbed water content the values of ε' and ε'' ncrease with increasing the sample temperature. At very low rate of sample thermal treatment first process is dominant and a monotone decrease of ε' and ε'' values is observed.

With increasing the sample thermal treatment rate we observe that the second process is dominant at the first stage. So, the values of ε' and ε'' increase with temperature. Later on, with continuing the increase of the sample thermal treatment rate, the second stage starts where the first process becomes dominant. Therefore, we observe the maximums on the some of experimental curves. Moreover, as the process of water molecule escape from the sample volume doesn't have an instantaneous character and it requires a time to take place, the temperature of observing the maximum on the experimental curve becomes higher and higher with increasing the sample thermal treatment rate.

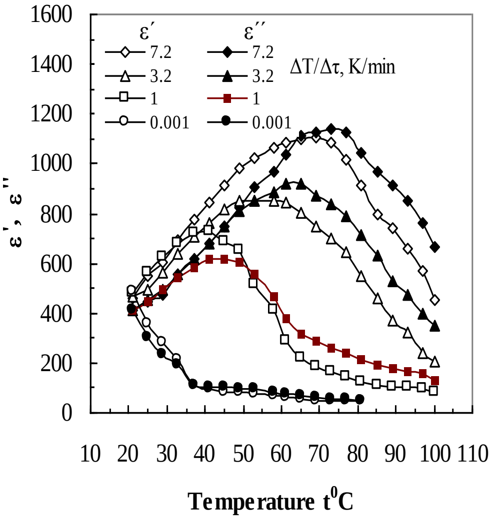

Fig.7. Temperature dependence of dielectric constant ε' and dielectric losses ε'' of natural clinoptilolite for different temperature increasing rate of sample.

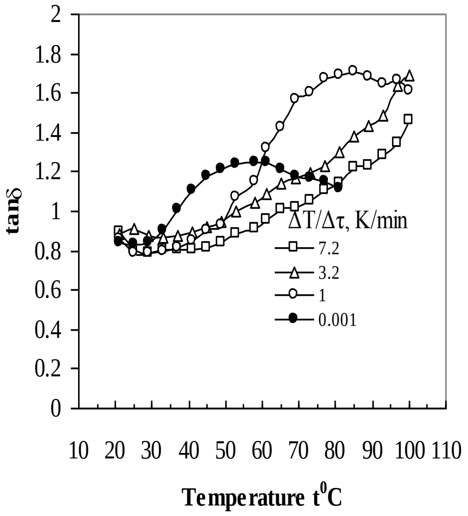

Fig.8. Temperature dependence of dielectric losses factor $\tan\delta = \varepsilon''/\varepsilon'$ natural clinoptilolite for different temperature increasing rate.

The dependence of dielectric losses factor $\tan\delta = \varepsilon''/\varepsilon'$ on increasing temperature rate of sample thermal treatment was also investigated. It is found that this factor changes also. At low temperature rates, a large maximum is observed while the character of $\tan\delta$ increase is monotone at high temperature rates.

On the base of obtained experimental data one can conclude that that the dielectric response of the studied zeolitic samples is due, in principal, to the water molecules absorbed by these samples. But this response is not the response of polar water molecules only as for water $\varepsilon' = 81$ while for the studied samples the experimental values of ε' are greater than that of water by one to two orders. So, we suppose that a part of absorbed water molecules decomposes as follows $H_2O \leftrightarrow OH^- + H^+$. On the other hand, OH^- creates with the cation an electric dipole. So, the zeolite dielectric response is due in principal to these dipoles. Moreover, one can suppose that the free proton H^+ is able to conduct electric current in the presence of external constant electric field. In the benefit of this supposition we can mention that the experimental results of measuring the dependence of dc current on the thermal treatment rate of the samples. The results are similar to those given in Figure 2. Moreover, after thermal treatment of the sample at high temperature (850^0C, for $100\,\text{min.}$), which leads, according to X-ray diffractometery, to the destruction of the crystalline structure of the zeolite elementary cell, We observed a strong decrease of dielectric parameters values ε' and ε'' (in several orders). So, on the base of the above experimental results, the process of water vapour absorption by zeolite could be presented as a two energetic level of a potential well (see Figure 9).

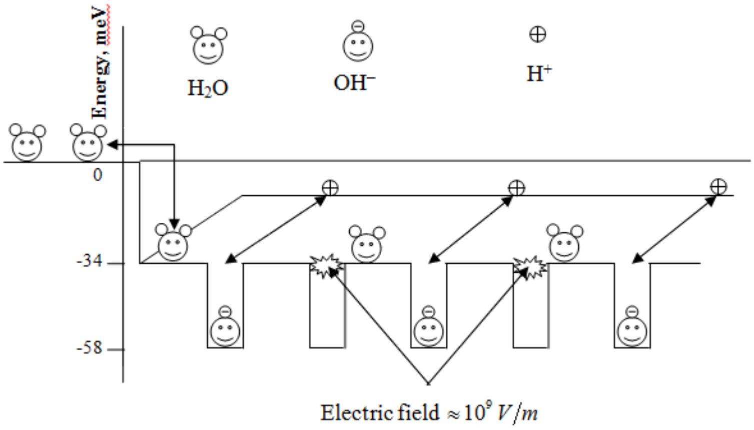

Fig.9. Presentation of hydration - dehydration processes of water molecules by clinoptilolite as a two-level potential well.

Preliminary modeling representation of the received results on hydration - dehydration processes is illustrated in fig.4. Accepting as zero value of potential energy of the water molecule in air the water absorption process can be presented by capture of molecules by potential well which consists of two levels. The first level (about $-34meV$) corresponds to macro porous in zeolite. The narrow wells correspond to micro-pores. The estimated calculations of well depth are carried out from thermogravimetric measurements data. Absorbed water going out from the sample volume at $t \approx 120^0 C$ and thermal energy of the water molecule will be $k_B T = -34eV$, where k_B - Boltzmann's constant, $T = 393K$ - absolute temperature.

It is known that in microspores of clioptilolite there are high electric fields about $10^9 V/cm$. Under the action of this field the polar molecules of water dissociate into ions $H_2O \leftrightarrow OH^- + H^+$. So, the generated protons (H^+) may form a dc electric current through a sample and OH^- may form electric dipole with cation which gives dielectric response.

Electric dipole = OH^- + Cation

All transition processes of water molecules from air into macro porous and back, and then captures by microspores some part of these molecules after dissociation and back take place in a dynamic mode. The dynamic balance condition at room temperatures is established for the investigated samples within several hours. The change of external factors (temperature $-T$, pressure $-P$, relative humidity $-\varphi$) the sample passes in a non-equilibrium condition.

3.2 Dc characteristics

Measurements of electro physical parameters were carried out on pressed samples. The samples are made of Syrian and Armenian natural zeolite powder (with grain size of 50 Micron). It should be noted that, after switching the constant electric field, the current passing through the sample is established at a time interval which gets beyond several hours sometimes (especially for large samples). This means that, in these cases, relaxation processes are taking place. The main reason for such relaxations is the polarization of the sample which can be taken into account by a well known method [11-13].

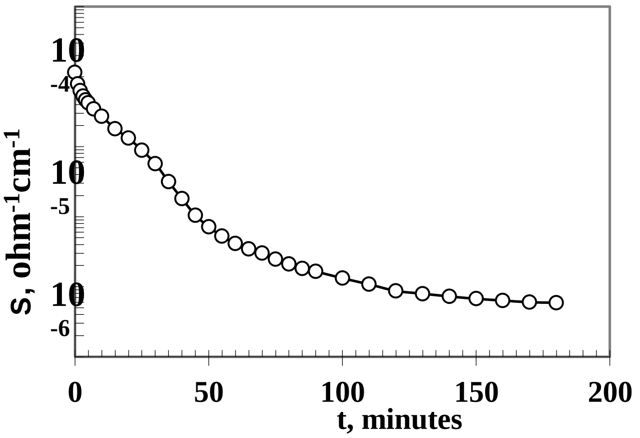

Fig. 10. The specific dc-conductivity dependence of the natural Armenian zeolite (clinoptilolite) on hydration time at temperature 24^0C.

We should mention here that during the period of storage, relative changes in the weight of the samples due to weather changes did not surpass 0.5%. The absolute accuracy in the weight measurement was $0.05mg$; hence the accuracy of measurement for σ is about 5%.

After having carried out the thermal treatment according to the above mentioned methodology, the dc conductivity of dried air samples was measured at a temperature equal to 24^0C 24^{o} C using a constant electrical field of $1\div3V/cm$. The weight of the sample was measured also with an absolute accuracy of $\pm0.05mg$.

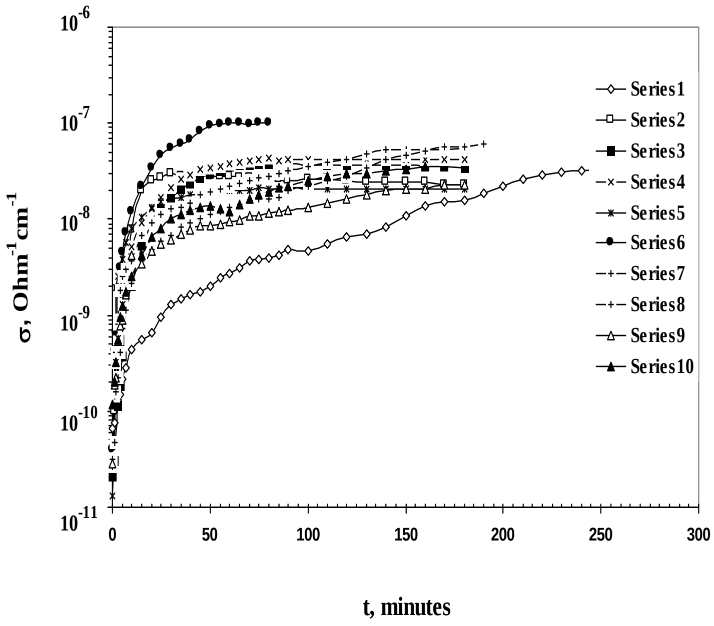

Fig. 11. The dependence of natural zeolitic samples specific conductivity on hydration time at temperature 24°C. **1**-A12; **2**-M5; **3**-2S14; **4**-4S14; **5**-6S14; **6**-8S14; **7**-10S14; **8**-12S14; **9**-16S14; **10**-20S14

In order to study the influence of the sample's water content on its dc-electrical conductivity, all the studied samples were put in a closed container for $4-5$ days at a saturated vapor pressure corresponding to a temperature equal to 24^0C. This procedure allows the samples to reach their state of total saturation. After that, each one of the studied samples was put in a special cell and its dc electrical conductivity was measured dynamically as a function of time at open air conditions. Thus, we could acquire the dependence of the dc conductivity on the dehydration degree. The dehydration degree is determined as $d_h = \frac{(m_0 - m)}{m_0} \cdot 100\%$, where m_0 is the mass of the sample with maximal water content and m is the current mass of the same sample. Some of the obtained results are given in Table 2. In addition, we present in Figure 10 the dependence of dc conductivity of Armenian sample $(A12)$ on the dehydration period length.

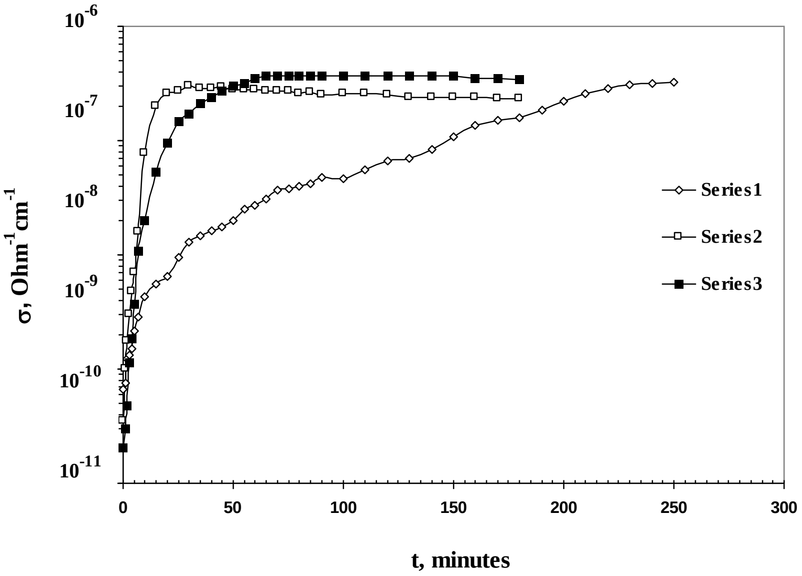

Fig. 12. The hydration time variation of the Specific conductivity of natural zeolitic samples (**1**-A12; **2**-M5; **3**-2S14) at temperature 24°C.

After dehydration, Syrian samples became unsuitable for measuring the dc conductivity since they conserved weakly their shape after the pressing. This is due, perhaps, to the inclusion of different phases in these samples (especially quartz and different zeolitic types). These samples could be destroyed when they reached total saturation. Therefore, the electrical conductivity of the Syrian samples was measured at the hydration mode, starting from partially dehydrated state up to totally dehydrated one. Therefore, the results corresponding to the state of total saturation are not given in Table 2 (see 2^{nd} column). We think that these data can be completed in the future after one finds suitable mode and pressing technology.

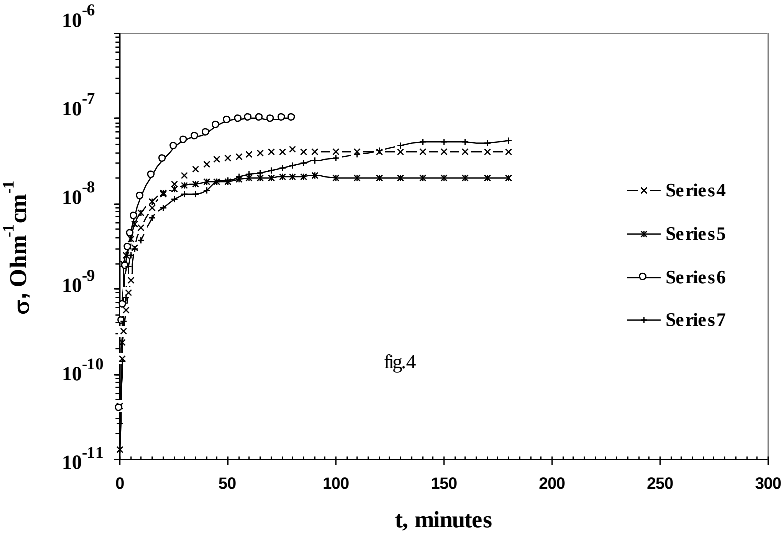

Fig 13. The hydration time variation of the Specific conductivity of natural Syrian zeolitic samples (**4**-4S14; **5**-6S14; **6**-8S14; **7**-10S14) at temperature 24°C.

It should be noted also that the dehydration degree (c.f. the 1st row in Table 2) is evaluated using for m_0 the value of the mass when the sample was at the state of total saturation. In contrast, the evaluation, in the other rows, was made using for m_0 the value at the partial dehydration state which corresponded to when the sample was thermally treated for two hours in open air conditions at temperature $220^0 C$. It is seen from Fig. 1 that the sample $A12$ reaches its equilibrium state within three hours, and here the dc conductivity becomes independent of time. In this case, the sample passes from total saturation state to dried-air state as a result of water emigration from the sample to the surrounding air. In other words, we have a dehydration sample at that time. This situation is accompanied by σ decrease from $1.2\cdot 10^{-5}\Omega^{-1}cm^{-1}$ to $6.77\cdot 10^{-9}\Omega^{-1}cm^{-1}$ in the case of Armenian samples. The measured values of dc electrical conductivity for all samples at some values of dehydration degree are presented in Table 2.

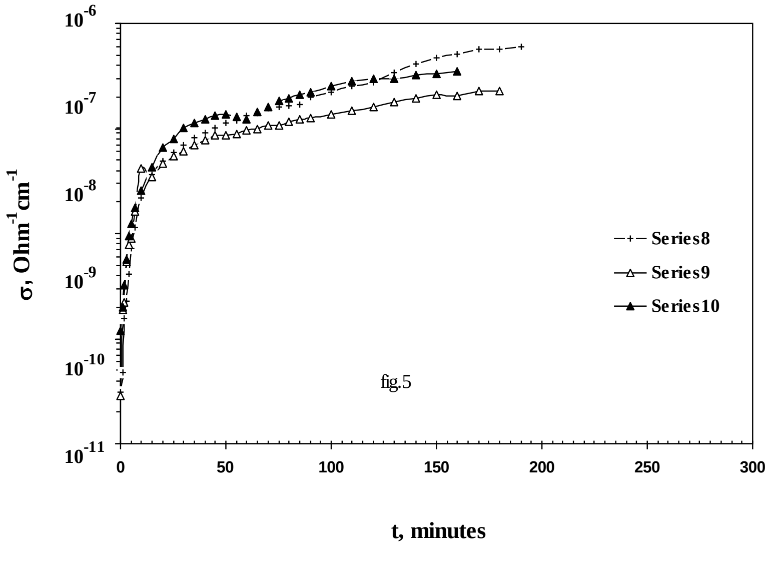

Fig.14. The hydration time variation of the specific conductivity of natural Syrian zeolitic samples (**8**-12S14; **9**-16S14; **10**-20S14) at temperature 24°C.

It is characteristic of sample $A12$ that the dependence of its conductivity on the water content in the mode of hydration differs from that of the hydration mode. This can be seen clearly by dividing the values of the dc conductivity, given in the 3^{rd} column of Table 2, by the corresponding values in the last (4^{th}) column in the same table to give the dc value of σ at the partially dehydrated state. In such a way, for Armenian samples, we find $(677/1.5=451)$ and $(1220/6.58=185)$ respectively. This behavior of conductivity at the mentioned two modes agrees well with the isothermal curves of sorption and desorption. For the Syrian samples, the following values were obtained (see Table 2, from top to bottom) $175; 575; 454; 1687; 998; 1600; 911; 521;$ and 145 respectively. The dependence of σ on the hydration time is illustrated in Figures 2-5. Figure 2 contains the data for all samples, whereas, for clarity and to make the comparison easier, the samples' data have been divided into groups and are presented in Fig. 12-14.

It is seen from Fig. 11-14 that with the increase of hydration time (i.e. with the increase of water content in the sample) the electrical conductivity of the samples increases until a definite moment when the increase stops. This moment is characteristic of each sample and it corresponds to the saturation state indicating that the hydration process has been finished and that the sample has reached its equilibrium state (air-dried sample). For some samples, this process goes relatively quickly (from 0.5 hour to 1 hour) while for others it goes more slowly. One can also notice additional stages on the curve of time dependence of electrical conductivity $\sigma(t)$. This is due, probably, to the inhomogeneous phase content of the corresponding samples.

Moreover, when comparing σ for natural Armenian and Syrian zeolitic samples one finds that during the process of establishing total hydration, the value of σ increases 2.5 times in magnitude for the Armenian samples, while for the Syrian samples, the same value triples its magnitude, and sometimes increases even more.

On the other hand, one can compute from Table 1, where the oxide contents of Armenian and Syrian samples is given, the molar ratio SiO_2/Al_2O_3 for these samples. When doing this, we find that this ratio is in the range $(3.17 \div 3.88)$ for the Syrian samples, while its value, for Armenian zeolite, could change in the range $(5.74 \div 5.91)$ [21- 27]. It is known [2,9,10] that samples with smaller values of this ratio are more conductive and less stable. Whence, the higher values of electrical conductivity of Syrian samples could be explained. However, it should be mentioned that, at relatively low temperatures, the measured values of σ and the stability of zeolitic samples are determined by their cation contents [1,9].

The mechanism of conductivity in zeolitic samples has a jumpy character and the ions or protons play, in general, the role of current carriers [1,2,5-7]. The content and the structure of the zeolitic sample determine its sorbitizing properties, in relation to water vapors [2,9,10]. Here, we found (see Fig. 15) that with the increase of water content, σ increases while the tilt of the curve of $\lg\sigma$ dependence on water concentration decreases. This means that the activation energy of conduction decreases also [2,9,10]. In our case, the availability of different tilts on the curve $\lg\sigma - t$ confirms this result.

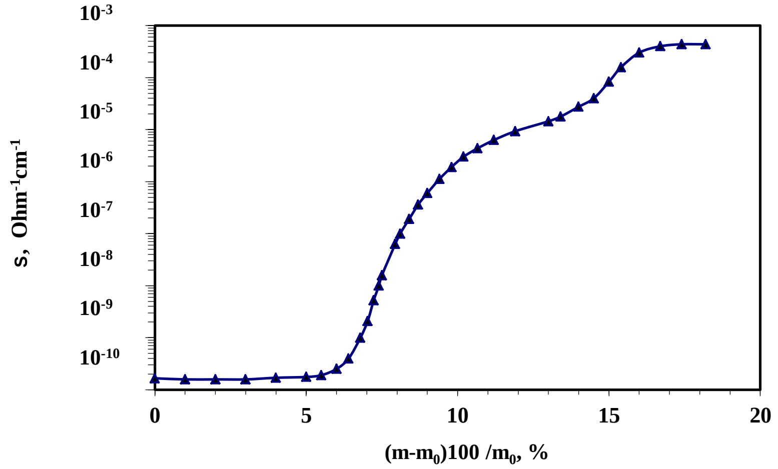

Fig.15. The dependence of dc-conductivity on water content.

Table 1: The chemical composition of the studied samples.

Sample	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	MgO	TiO_2	Mn_2O_3	Cr_2O_3	P_2O_5	L. I.
A12	67.11	11.69	0.79	2.22	4.9	2.23	1.28	0.20	-	-	-	14.19
2S14	39.51	10.48	1.22	1.01	8.77	11.68	12.21	1.60	0.2	0.03	0.44	12.3
4S14	38.69	9.98	0.93	0.89	11.01	10.41	11.09	1.48	0.17	0.03	0.46	14.10
6S14	37.64	10.15	0.99	1.08	11.92	10.65	9.74	1.60	0.17	0.03	0.52	15.16
8S14	37.14	9.80	0.75	0.84	14.95	8.97	8.55	1.37	0.15	0.03	0.52	16.52
10S14	39.95	10.42	1.13	1.02	6.73	13.20	14.17	1.64	0.22	0.04	0.41	10.98
12S14	40.76	11.65	1.50	1.13	8.24	12.02	9.99	1.84	0.20	0.03	0.49	10.46
M5	40.17	10.97	1.66	1.13	8.95	11.75	10.65	1.75	0.18	0.03	0.47	10.71
16S14	41.36	13.04	1.45	1.24	8.26	12.60	9.01	2.10	0.20	0.03	0.52	9.28
18S14	41.08	12.00	1.43	1.19	8.18	11.99	10.45	1.92	0.19	0.03	0.49	9.31
20s14	41.23	11.63	1.65	1.18	7.96	12.30	10.62	1.87	0.19	0.03	0.47	9.24

Table 2: Specific electrical conductivity at T=24^0 C for natural Armenian (A12) and Syrian (M and S) zeolites corresponding to different degrees of dehydration d_h.

samples	σ (in 10^{-11} $\Omega^{-1}cm^{-1}$) for corresponding degree of dehydration (in %)		
A12	1200000 for d_h=0	677 for d_h=9.22	1.5 for d_h=14.8
A12	-	1220 at ambient air	6.58 for d_h=5.73
M5	-	618 at ambient air	3.52 for d_h=6.65
2S14	-	1190 at ambient air	2.07 for d_h=5.32
4S14	-	1930 at ambient air	4.25 for d_h=4.8
6S14	-	2210 at ambient air	1.31 for d_h=6.4
8S14	-	4030 at ambient air	4.04 for d_h=4.3
10S14	-	4290 at ambient air	2.68 for d_h=6.16
12S14	-	2860 at ambient air	3.14 for d_h=7.4
16S14	-	1480 at ambient air	2.84 for d_h=5.52
20S14	-	1730 at ambient air	11.9 for d_h=5.3

4. Conclusions

Finally it should be noted here that the main results obtained in this work are:

- The dielectric constant ε' and the dielectric loss ε'' of all studied samples decrease when we increase the frequency of applied electrical field. This finding agrees well with the finding of other works and could be taken as a characteristic for natural zeolites and synthetic ones.
- The dielectric response of zeolites is highly sensitive to the water content of samples.
- $\tan\delta = \varepsilon''/\varepsilon'$ for all studied samples differs significantly from one sample to another in both its value and the character of the low frequency dependence of the applied electrical field.
- The obtained frequency dependence of alternative current (ac) conductivity σ_{ac} of the studied samples agrees well with the finding of others.
- $\tan\delta$ characterizes electrical dipole moments of the studied materials and constitutes a source of information for the structural changes in these dipoles and their ambiance surrounding.
- Finally, we can conclude that the complete explanation of the observed phenomena requires the measured values of σ in a more wide range of temperature, hydration and studied samples, which should be modified using different chemical and radiation methods [5-7,21-25]. These results should also accompanied by the results of other related physical measurements. We have to mention also that the measurement of surface conductivity in addition to the volume conductivity could give a possibility of understanding many phenomena especially the process of sorption which passes through surface. Nowadays, we do this kind of measurement and the preliminary results show that it is high sensitive to the humidity and temperature in comparison with the volume conductivity.

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