Dielectric spectroscopy of some heteronuclear amino alcohol complexes

Mamdouh S. Masoud [a], Medhat A. Shaker [b], Alaa E. Ali [b],*

[a] *Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt*
[b] *Physics and Chemistry Department, Faculty of Education, Damanhour, Alexandria University, Egypt*

Abstract

The temperature dependent dielectric spectroscopic properties of two heteronuclear complexes of monoethanolamine (MEA) at a wide temperature range (303–413 K) were investigated by impedance spectroscopy, in the frequency range from 100 Hz to 100 kHz. The frequency dependence of the impedance spectra plotted in the complex plane shows semi-circles. The Cole–Cole diagrams have been used to determine the molecular relaxation time, τ. The temperature dependence of τ is expressed by thermally activated process. Relaxation frequencies corresponding to the rotation of the molecules about their long axes are expected to lie above 10 MHz and exhibit Arrhenius behavior, where a single slope is observed with activation energy values equal to 0.67 and 0.78 eV. The ac conductivity σ_{ac} (ω) is found to vary as ω^s with the index $s \leq 1$, indicating a dominant hopping process at low temperatures. The dielectric permittivity dependence as a function of frequency and temperature have been determined and showed a strong dispersion at frequency lower than 10 kHz. Capacitance and losses, tan δ, decreased with increasing frequency and increased with increasing temperature. The analysis of the data reveals that such characteristics are in good agreement with semi-conducting features based mainly on the hopping mechanism.
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Keywords: Amino alcohol complexes; Dielectric properties; Permittivity and loss; Dielectric relaxation; Arrhenius plot

1. Introduction

Ethanolamines are versatile ligands containing amine and alcohol groups that readily form coordination compounds with almost all metal ions and behave as N- and O-donor ligands. Their structural chemistry has been investigated in depth using different spectroscopic and thermal techniques. Their bifunctional nature enables them to serve a variety of commercial applications such as corrosion inhibitors, surfactants, gas purification and herbicides [1]. Recently, aqueous ethanolamines remain as the principal acid gas absorbents and comprise 40% of the market [2]. Homo- and hetero-bimetallic ethanolaminate derivatives of a number of metals have been reported recently [3–5]. Dielectric spectroscopy (DS) is an old experimental tool, which has dramatically developed in the last two decades. It covers nowadays the extraordinary spectral range from 10^{-6} to 10^{12} Hz. This enables researchers to make sound contributions to contemporary problems in modern physics. The complex dielectric function describes the interaction of electromagnetic waves with matter and reflects by that the underlying molecular mechanisms. It is known that dielectric study can reveal many information of a solid, such as phase transition, defect, and transport properties. A detailed analysis of the frequency and temperature dependence of the ac conductivity and permittivity is necessary in order to characterize the microscopic mechanisms and the accompanied relaxation phenomena of the charge carrier transport. Dielectric spectroscopy is a non-invasive, very sensitive technique to investigate complex systems in general and is particularly suitable to study biological systems as recently reviewed [6–10]. For the investigation of relaxation processes and conductivity dielectric spectroscopy is a frequently used method. Dielectric relaxation spectroscopy (DRS) is a popular and powerful technique that has been shown to provide information about the molecular dynamics of almost any kind of materials and liquid crystals [11,12]. In particular, dielectric measurements complement dynamic mechanical analysis (DMA), for example, by determining the frequency dependence of the various processes over a wider range of frequencies. As a part of our ongoing research on the synthesis, spectral, thermal and structural analysis of mono-, di- and triethanolamine complexes with of most classes of metals [13–23], we report in this paper the dielectric properties of the $CoNi(MEA)_2Cl_2 \cdot H_2O$ and $CoCu_2(MEA)_2Cl_4 \cdot H_2O$

* Corresponding author.
E-mail address: dralaae@yahoo.com (A.E. Ali).

complexes as a function of both temperature and frequency. This gives deeper insight into the structure of these complexes. We measured the frequency dependence of the ac conductivity and the dielectric permittivity of these complexes as a function of temperature. Using the electric modulus representation, the conduction behavior of these samples was characterized over a wide range of frequency and temperature. Moreover, the conductivity and dielectric permittivity relaxation processes have been discussed.

2. Experimental

The solid metal monoethanolamine (MEA) heteronuclear complexes were prepared by mixing 0.1 mol of the metal salts (Co^{II}, Ni^{II}, Cu^{II} as chloride) dissolved in 10 ml of water with the calculated amount of the MEA ligand saturated with ethanol to obtain 1:1:2 and 1:2:2 (M_1:M_2:MEA) ratios. The mixture was refluxed for about 5 min. The complexes were precipitated and were filtered, then washed several times with a mixture of EtOH–H_2O and dried in a desiccator over anhydrous $CaCl_2$. The metal ion contents were determined by complexmetric titration procedures [24]. The halogen content was determined by titration with standard $Hg(NO_3)_2$ solution using diphenyl carbazone indicator [25]. The structural identification of the complexes (Fig. 1) was reported [26].

The complexes were pressed into discs of 10 mm diameter and 1–2 mm thickness at a pressure of 9.8×10^8 Pa. Silver paste was painted on the major faces of each test piece as electrodes. The Permittivity ε' and dielectric loss ε'' of the investigated compounds were measured using HP 8510C Vector Network Analyzer with the help of a HP 8507B dielectric probe kit in the frequency range 100 Hz–100 kHz. The dielectric measurements were performed by employing the time domain reflectometry (TDR) technique. The accuracy in the measurement of ε' and ε'' values obtained from the Network Analyzer and TDR technique is within ±2% and ±5%, respectively. All these measurements were carried out at (303–413 K) temperature range and the temperature being controlled thermostatically within ±0.5 K.
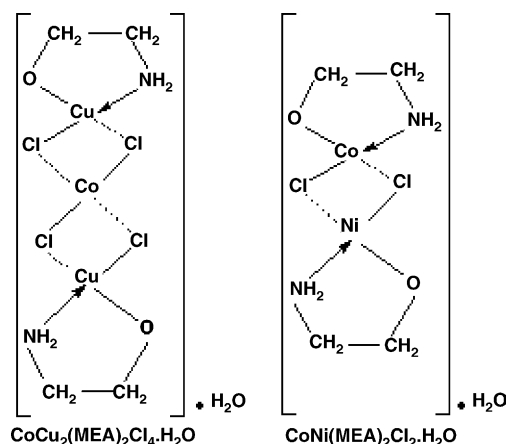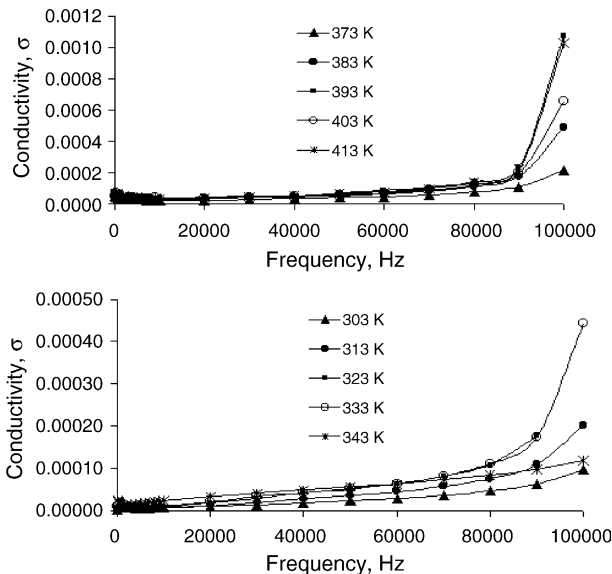

Fig. 1. The structures of the investigated complexes.

Fig. 2. The frequency dependence of the total conductivity, σ for the $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex at different temperatures.

3. Results and discussion

The total conductivity, σ, the dielectric loss, tan δ, Cole–Cole and impedance diagrams have been studied in the temperature range (303–413 K) and frequency range (100 Hz–100 kHz) for the $CoNi(MEA)_2Cl_2 \cdot H_2O$ and $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complexes. The frequency dependence of the total conductivity, σ for the $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex at different temperatures is illustrated in Fig. 2. It is noticed that the general behavior shows a nearly frequency independent values of σ at low frequency range, while a strong frequency dependence appears at high frequency range followed by a stationary value. The transition point between the nearly independent and that of the strong dependence regions is shifted towards higher frequency with increasing temperature. At the high frequency range, the conductivity obeys a power relation:

$$\sigma(\omega) = A\omega^s$$

where ω is the angular frequency; A, a is frequency independent parameter; and s is a power where $s \leq 1$, indicating a dominant hopping process at low temperatures. At low frequency range, the conductivity refers to the dc conductivity of the investigated complex (extrapolation of $\sigma(\omega)$ to $\omega = 0$). Thus, the total conductivity [27] could be given by:

$$\sigma = \sigma_{dc} + A\omega^s$$

For the complex $CoNi(MEA)_2Cl_2 \cdot H_2O$, the frequency dependence of the total conductivity, σ is shown in Fig. 3. It is noticed that the general behavior shows high frequency dependent values of σ at all frequency range and strong frequency dependence appears at high frequency range. The complex permittivity $\varepsilon^*(\omega)$ can be expressed as a complex number:

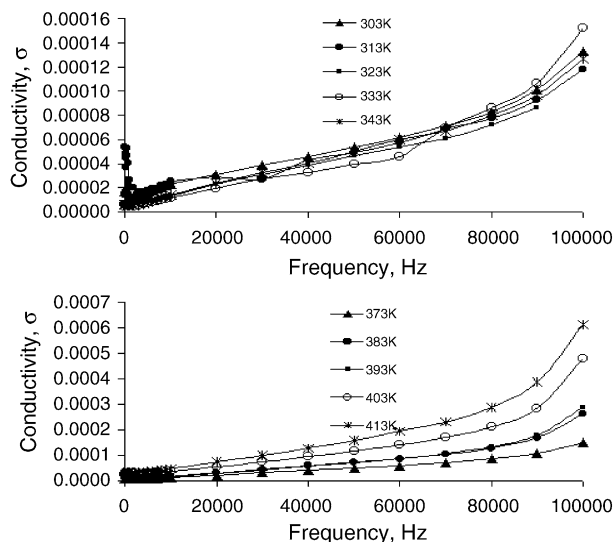$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

Fig. 3. The frequency dependence of the total conductivity, σ for the CoNi(MEA)$_2$Cl$_2\cdot$H$_2$O complex at different temperatures.
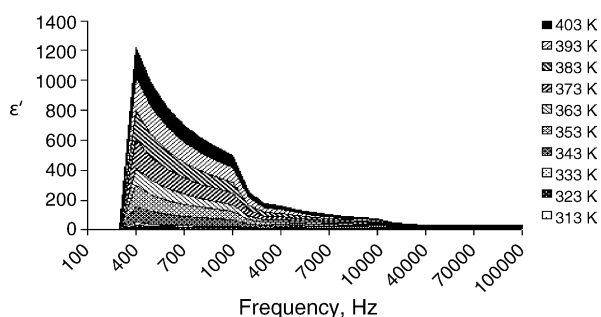
Fig. 4. The Variation of dielectric permittivity ε' of the CoCu$_2$(MEA)$_2$Cl$_4\cdot$H$_2$O complex as a function of frequency at different temperatures.

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary parts of the complex permittivity, respectively.

Figs. 4 and 5 show the variation of real part of permittivity, ε', as a function of frequency at several temperatures for the investigated complexes. The ε' parameter was derived from impedance measurements in a conventional way, according to the following
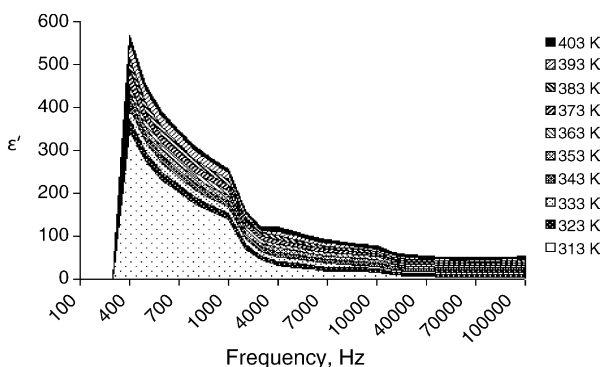

Fig. 5. The Variation of dielectric permittivity ε' of the CoNi(MEA)$_2$Cl$_2\cdot$H$_2$O complex as a function of frequency at different temperatures.
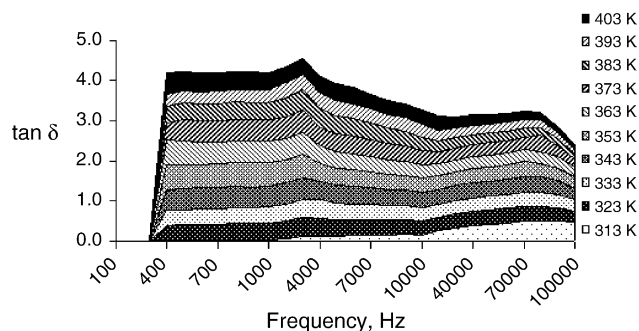

Fig. 6. Dielectric losses, $\tan\delta$, as a function of frequency for the CoNi(MEA)$_2$Cl$_2\cdot$H$_2$O complex at several temperatures.

equation:

$$\varepsilon'(\omega) = \frac{Z''(\omega)}{\omega\varepsilon_0 A|Z|^2}$$

where A is the geometric factor and $|Z|^2$ is the impedance modulus. A high degree of dispersion of the permittivity is identified at high temperatures and low frequencies. This behavior was for dielectric materials, in which a hopping type mechanism of conduction is present [28]. It may be noted that for the studied complexes, there is a decrease in the dielectric constant with increasing frequency, which is a typical characteristic of normal dielectric [29]. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field because charges possess inertia [29]. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant. Also, the variation of dielectric permittivity is noticed with increasing the temperature.

Figs. 6 and 7 show the tangent losses, $\tan\delta$, as a function of frequency at several temperatures. It is noticed that the real part of dielectric function changes with the frequency in a monotonic way, whereas its tangent losses (Figs. 6 and 7) show a maximum. Whenever a maximum or peak is spotted, it is desirable to locate its frequency position, as well as its width for a particular dielectric function. For the CoNi(MEA)$_2$Cl$_2\cdot$H$_2$O complex, Fig. 6, all the curves show an intense increase of the loss magnitude below 4 kHz. At high frequencies, the losses are much lower than one occurring at low frequencies. This kind of dependence of the
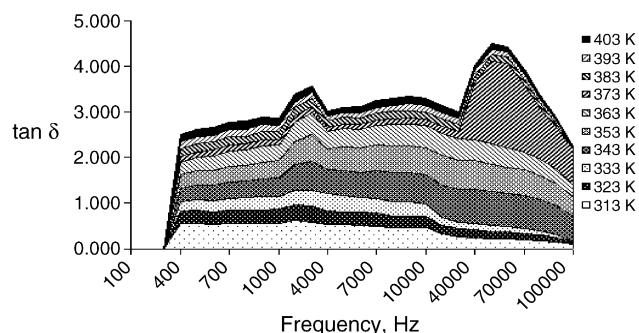

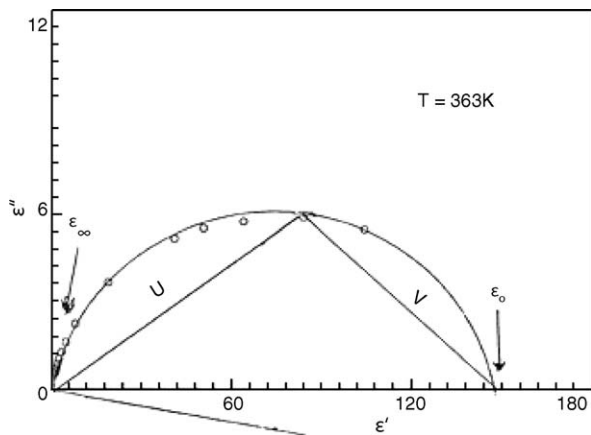Fig. 7. Dielectric losses, $\tan\delta$, as a function of frequency for the CoCu$_2$(MEA)$_2$Cl$_4\cdot$H$_2$O complex at several temperatures.

Fig. 8. The Complex permittivity diagram for the $CoCu_2(MEA)_2Cl_4\cdot H_2O$ complex at 363 K.

$\tan\delta$ with frequency is associated with losses due to the conduction mechanism. For the $CoCu_2(MEA)_2Cl_4\cdot H_2O$ complex, Fig. 7, all the curves below 110 °C show an intense increase of the loss magnitude below 4 kHz while above this temperature another more intense increase of the loss magnitude below 7 kHz appears. Also, at higher values than these two frequencies the losses values are much lower than those occurring at these low frequencies.

A representative example for the dependence of the dielectric constant $\varepsilon'(\omega)$ on the dielectric loss $\varepsilon''(\omega)$ at certain temperature is shown in Fig. 8.

The locus ε', real value of permittivity, and ε'', imaginary value of permittivity, for various frequencies in rectangular axes of coordinates ε', ε'' should form a semi-circle for polar compounds, with the center lying axis with coordinates $(\varepsilon_0 \pm \varepsilon_\infty)/2$ [29]. ε_0 is the static permittivity at direct voltage and ε_∞ is the optical permittivity for very high frequencies approaching the frequencies of light oscillators [30]. The dielectric loss, $\tan\delta$, value depends on various external factors. The behavior of the dielectric loss at the low frequencies is related to the character of the phase transition. In some cases, nucleation of a new phase and the further growth of the nuclei are regarded as the main source of the peak value for $\tan\delta$ at the phase transition temperature. The familiar dielectric function, ε, may be expressed in terms of: $\varepsilon = \varepsilon' - i\varepsilon''$ where $(i = \sqrt{-1})$. A semi-circle is obtained on plotting ε' against ε'' for each temperature. The centers of the semi-circles lie below the abscissa axes. This semi-circle Cole–Cole diagram has been used to determine the distribution parameter α, the macroscopic relaxation time τ_0 and the molecular relaxation time τ [30,31]. Knowing α, τ_0 can be determined using the relation: $U/V = (\omega\tau_0)^{1-\alpha}$ where U is the distance on the Cole–Cole diagram between the static dielectric constant ε_0 and the experimental point, V is the distance between that point and the optical dielectric constant, ε_∞ and ω is the angular frequency, $\omega = 2\pi\upsilon$. The parameter α equals zero when the compound has only one relaxation time, whereas, for a series of relaxation times, the value of α varies between 0 and 1. The extent of the distribution of relaxation times increases with increasing parameter α. On the other hand, the value of τ_0 decreases with increasing temperature [31]. The molecular relaxation time τ could be determined based on the following equation [31]:

$$\tau = \frac{2\varepsilon_0 + \varepsilon_\infty}{3\varepsilon_0}\tau_0$$

The temperature dependence of τ can be expressed by a thermally activated process in the frame of an Arrhenius concept of the type [32,33]:

$$\tau = \tau_0 \exp\left(\frac{E_0}{kT}\right)$$

where τ_0 is a constant characteristic of the relaxation time and represents the time of a single oscillation of a dipole in a potential well; E_0, the energy of activation for the relaxation of the dipole; and τ represents the average or most probable value of the spread of the relaxation times. From the analysis of the dielectric data of the investigated complexes, the relationships between the different dielectric parameters are obtained and are given in Tables 1 and 2. By comparing the dielectric properties of the $CoNi(MEA)_2Cl_2\cdot H_2O$ and $CoCu_2(MEA)_2Cl_4\cdot H_2O$ complexes, the effect of changing the central metal ion on both complexes can be seen. In both complexes the relative permittivity values increase with increasing temperature. The data are fairly in harmony with the physical properties of the metal, especially from its electronic structure. The observed val-

Table 1
Dielectric parameters obtained from the analysis of Cole–Cole diagrams for the $CoCu_2(MEA)_2Cl_4\cdot H_2O$ complex

Temperature (K)	U	V	ϕ	α	Frequency (υ)	τ_0 (s)	ε_0	ε_∞	τ (s)
303	3.4	3.5	30	19.1	900	5.1E−06	96	1	3.1E−02
313	3.2	2.8	20	12.7	1000	1.5E−06	120	3	1.5E−02
323	2.8	2.2	38	24.2	900	4.8E−07	136	9	6.1E−03
333	3.7	1.7	32	20.4	1000	2.7E−07	146	4	3.8E−03
343	3.7	2.9	18	11.5	900	1.9E−07	120	7	1.9E−03
353	3.7	2.8	27	17.2	900	5.6E−08	150	12	8.8E−04
363	3.6	2.7	35	22.3	800	3.8E−08	145	8	5.5E−04
373	4.0	0.8	43	27.4	3000	3.0E−08	155	3	4.9E−04
383	2.6	1.2	53	33.8	2000	1.7E−08	130	6	2.0E−04
393	5.1	1.1	52	33.1	2000	6.1E−09	177	22	1.4E−04
403	5.5	4.0	31	19.7	500	2.4E−09	182	41	5.8E−05
413	3.2	1.2	54	34.4	2000	3.2E−09	150	13	5.0E−05

Table 2
Dielectric parameters obtained from the analysis of Cole–Cole diagrams for the $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex

Temperature (K)	U	V	Angle	α	Frequency (υ)	τ_0 (s)	ε_0	ε_∞	τ (s)
303	3.1	1.5	32	20	2000	4.8E−06	102	2	3.4E−02
313	4.4	3.3	16	10	1000	6.8E−07	173	7	1.4E−02
323	4.4	2.1	30	19	2000	4.0E−07	144	8	5.7E−03
333	4.3	1.8	38	24	6000	2.4E−07	122	6	2.4E−03
343	3	2	35	22	8000	1.1E−07	119	12	1.1E−03
353	4.4	1.9	29	18	7000	5.6E−08	114	14	5.2E−04
363	3.7	3.5	26	17	700	1.4E−08	180	6	3.0E−04
373	2.8	1.2	40	26	4000	6.8E−09	160	2	1.2E−04
383	4.6	2.1	30	19	4000	9.7E−09	119	1	9.2E−05
393	3.8	2.8	33	21	800	2.3E−09	154	11	3.8E−05
403	4.7	1.7	35	22	10000	2.0E−09	111	9	1.7E−05
413	5.6	1	27	17	20000	3.9E−09	66	5	1.2E−05

ues of static dielectric constants, ε_0 for $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex are higher than those for $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex at all temperatures, Tables 1 and 2. The higher values of ε_0 for $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex in comparison to $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex is due to its larger molecular weight. The dielectric dispersion of the investigated complexes is described by Cole–Cole equation. The dielectric behavior of $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex exhibits a Debye type relaxation [34]. The Debye process suggests the cooperation process involving the relaxation of the structure i.e. the case of molecules around any particular individual [35,36]. The observed value of relaxation time, τ_0 for $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex is much higher in comparison to the τ_0 value of $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex at the same temperature. This suggests that the molecular reorientation of associated $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ molecules is highly restricted due to its more complicated molecular structure. In conclusion, the relative permittivity and dielectric loss values for the investigated complexes indicate a dipolar mechanism of polarization. The data reveal semi-conducting features based mainly on the hopping mechanism.

Fig. 9 represents the reciprocal temperature dependence of the conductivity relaxation time that obeys the Arrhenius expression. The activation energy E_0 for the relaxation process obtained from the least-squares straight-line fits is in good agreement with the activation energy for the dc conductivity
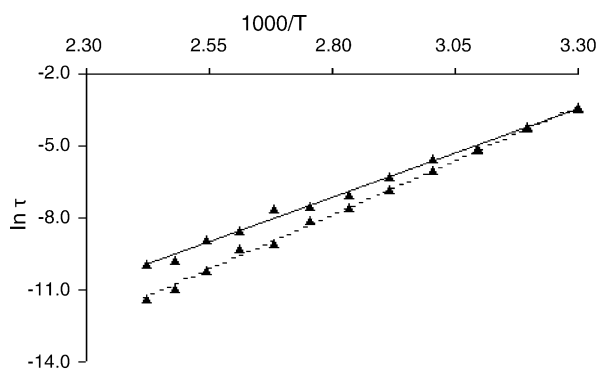
of the complexes. The obtained E_0 values equal 75.6 kJ/mol (0.78 eV/molecule) for the $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex and 64.6 kJ/mol (0.67 eV/molecule) for the $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex.

Fig. 9. Arrhenius plots of the relaxation times from dielectric measurements: straight line for $CoCu_2(MEA)_2Cl_4 \cdot H_2O$ complex and dashed line for $CoNi(MEA)_2Cl_2 \cdot H_2O$ complex.

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