

Dielectric spectroscopy of some heteronuclear amino alcohol complexes

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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 $\sigma_{ac}(\omega)$ 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, $\tan \delta$, 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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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 ethanolamine 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 mat-

ter 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 $\text{CoNi}(\text{MEA})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{CoCu}_2(\text{MEA})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$

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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 ($\text{M}_1:\text{M}_2:\text{MEA}$) ratios. The mixture was refluxed for about 5 min. The complexes were precipitated and were filtered, then washed several times with a mixture of $\text{EtOH}-\text{H}_2\text{O}$ and dried in a desiccator over anhydrous CaCl_2 . The metal ion contents were determined by complexometric titration procedures [24]. The halogen content was determined by titration with standard $\text{Hg}(\text{NO}_3)_2$ 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 $\pm 2\%$ and $\pm 5\%$, respectively. All these measurements were carried out at (303–413 K) temperature range and the temperature being controlled thermostatically within ± 0.5 K.

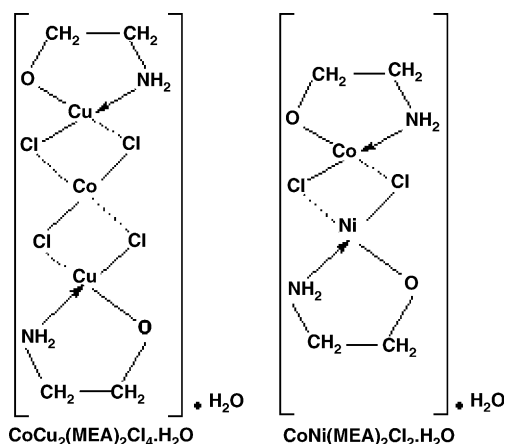


Fig. 1. The structures of the investigated complexes.

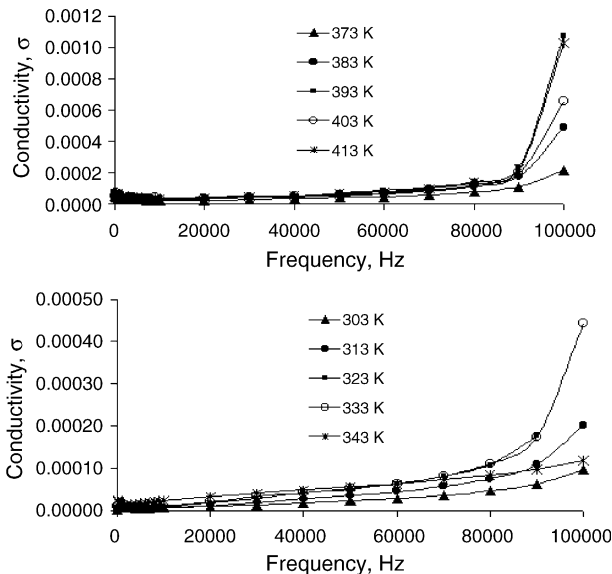


Fig. 2. The frequency dependence of the total conductivity, σ for the $\text{CoCu}_2(\text{MEA})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ complex at different temperatures.

3. Results and discussion

The total conductivity, σ , the dielectric loss, $\tan \delta$, Cole–Cole and impedance diagrams have been studied in the temperature range (303–413 K) and frequency range (100 Hz–100 kHz) for the $\text{CoNi}(\text{MEA})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{CoCu}_2(\text{MEA})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ complexes. The frequency dependence of the total conductivity, σ for the $\text{CoCu}_2(\text{MEA})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ 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 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:

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

For the complex $\text{CoNi}(\text{MEA})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$, 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 $\epsilon^*(\omega)$ can be expressed as a complex number:

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

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