Dielectric properties of some cadmium and mercury amino alcohol complexes at low temperatures

MAMDOUH S. MASOUD[a], AHMED M. HAFEZ[b], M. SH. RAMADAN[a] and ALAA E. ALI[c]

[a]*Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt,* [b]*Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt and* [c]*Physics & Chemistry Department, Faculty of Education "Damanhour", Alexandria University, Egypt*
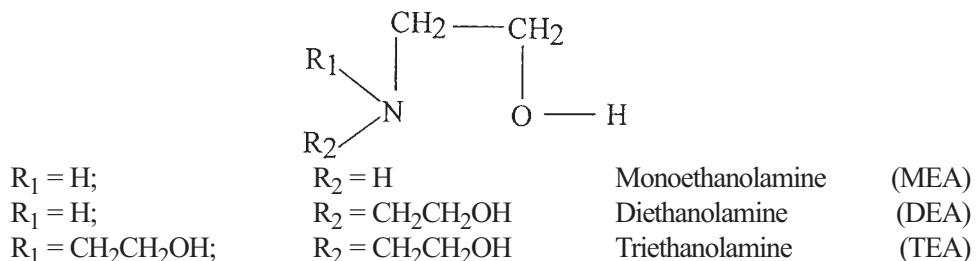
Abstract: The dielectric properties of some cadmium and mercury amino alcohol complexes were studied within the temperature range of 100–300 K at the frequencies of 100, 300 and 1000 kHz. The polarization mechanisms are suggested and the dependence of both ε and tg δ on both temperature and frequency are analyzed. The analysis of the data reveals semi-conducting features based mainly on the hopping mechanism.

Keywords: amino alcohol complexes, Hg, Cd, dielectric properties.

INTRODUCTION

Amino alcohol complexes find progressive application in different fields: buffers,[1] catalysts,[2] inhibitors,[3] ion exchangers,[4] additives in building materials,[5] electroplating[6] and dyes.[7] In our laboratory, their structural chemistry have been investigated in depth using different spectroscopic and thermal methods of analysis.[8–24] As a continuation of this work, the dielectric properties of the entitled complexes were studied as a function of both temperature and frequency. This gives deeper insight into the structure of these complexes. The following skeleton is given for the ligands:

$R_1 = H$;	$R_2 = H$	Monoethanolamine	(MEA)
$R_1 = H$;	$R_2 = CH_2CH_2OH$	Diethanolamine	(DEA)
$R_1 = CH_2CH_2OH$;	$R_2 = CH_2CH_2OH$	Triethanolamine	(TEA)

EXPERIMENTAL

The solid metal-amino alcohol complexes were prepared by mixing the required weight of the metal salt (Cd^{II} and Hg^{II}) dissolved in the least amount of water with the calculated amount of the ligand saturated with ethanol. The mixture was refluxed for about 5 min. The complexes were precipitated and filtered, washed several times with a mixture of EtOH–H$_2$O solvent and then dried in a vacuum desiccator over anhydrous CaCl$_2$.

The metal ion contents were determined by complexometric titration procedures.[25,26] The halogen content was determined by titration with a standard Hg(NO$_3$)$_2$ solution using diphenyl carbazone as the indicator,[24,25] the sulphate content was determined gravimetrically as BaSO$_4$.[26] The analytical data and m.p. of the prepared complexes are collected in Table I.

TABLE I. Analytical data and m.p. (ºC) of the metal amino alchol complexes.

Complex	Geometry	M.p./ºC	% Found (% Expected)		
			M	Cl	SO$_4$
Cd(MEA)SO$_4$	*Td*	> 300	41.1	–	35.5
			(41.1)		(35.6)
Cd(MEA)$_2$SO$_4$	*Oh*	265	34.3	–	29.0
			(34.4)		(29.0)
Cd(DEA)SO$_4$	*Td*	225	35.8	–	30.5
			(35.8)		(30.6)
Cd(DEA)$_2$SO$_4$	*Oh*	200	26.8	–	22.9
			(26.8)		(22.9)
Cd(TEA)SO$_4$	*Td*	220	31.4	–	26.8
			(31.4)		(26.8)
Cd(TEA)$_2$SO$_4$	*Oh*	> 300	22.1	–	18.9
			(22.2)		(18.9)
Hg(MEA)$_2$Cl$_2$	*Oh*	290	50.9	18.1	–
			(50.9)	(18.0)	
Hg(DEA)$_2$Cl$_2$	*Oh*	200	41.6	14.7	–
			(41.6)	(14.7)	

Td = Tetrahedral, *Oh* = Octahedral

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 measurements of the permittivity and the dielectric loss were performed at the frequencies of 100, 300 and 1000 kHz in the temperature range 100–300 K using an LCR meter (4275A) (Institute of Physics, A. Mickiewicz University, Poznan, Poland).

RESULTS AND DISCUSSION

The permittivity values of the *Td* [Cd(MEA)SO$_4$] complex, Fig. 1, were constant up to 215 K, after which they increased successively with increasing temperature, the relative permittivity values ranged from 10 to 70. The behaviour of the dielectric loss values indicates a polar polarization mechanism, where its values are affected by both temperature and frequency, Fig. 1. However, the relative permittivity values of the *Oh* [Cd(MEA)$_2$SO$_4$]

Fig. 1. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Td* [Cd(MEA)SO$_4$] complex.

Fig. 2. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Oh* [Cd(MEA)$_2$SO$_4$] complex.

complex, Fig. 2, are in the range of 10–50, *i.e.*, less than that of the *Td* [Cd(MEA)SO$_4$] complex. This remarkable feature was observed for both the mono- and triethanolamine complexes, Figs. 1, 2, 5 and 6. This finding is opposite to that of the zinc complexes.[27] Comparing the behaviour of the diethanolamine complexes, Figs. 3 and 4, it is found that both ε and tg δ are higher in case of the *Td* complex than those of the *Oh* complex. This may be due to the *Td* complex existing in two different phases. This is confirmed from the sudden drop in the ε values at 150–160 K.

In a similar way, the following conclusions can be made for the mercury complexes:

i) The ε values of the *Oh* [HgL$_2$Cl$_2$] complexes, L = MEA, DEA, Figs 7 and 8, ranged between 4.5–8.0 and 4.0–4.4 for MEA and DEA complexes, respectively. Such values increase with increasing temperature and decrease with increasing frequency.

ii) The dielectric loss values of the *Oh* [Hg(MEA)$_2$Cl$_2$] complex, Fig. 7, ranged from zero to 0.15, increasing with increasing temperature and decreasing with increasing frequency.

iii) The dielectric loss values of the *Oh* [Hg(DEA)$_2$Cl$_2$] complex, Fig. 8, are very small ($\approx$0.025) and are affected by neither temperature nor frequency.
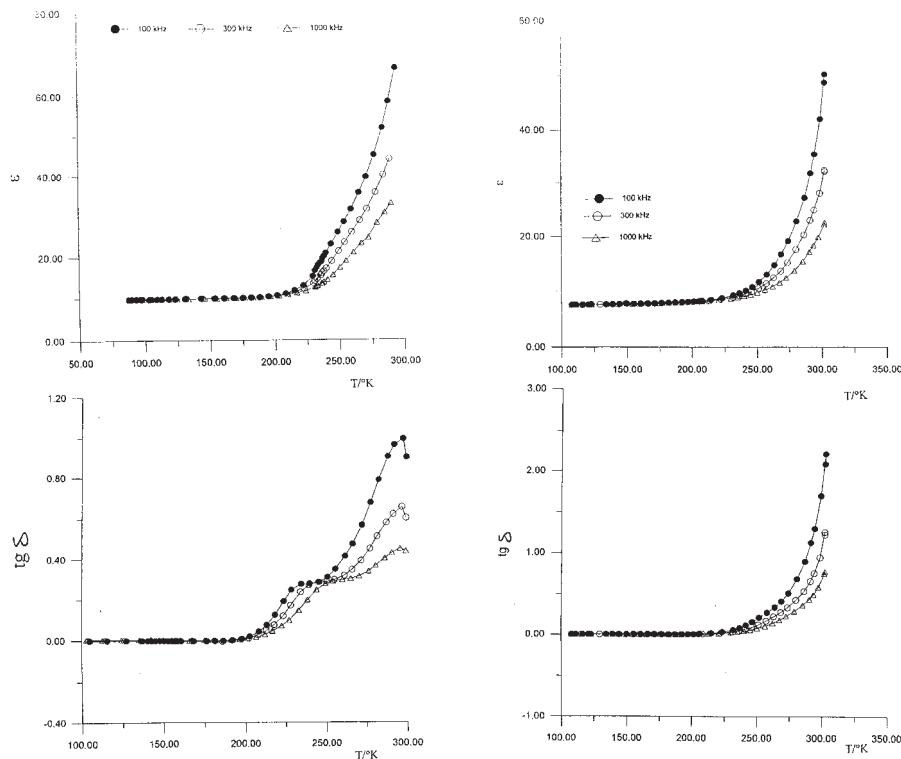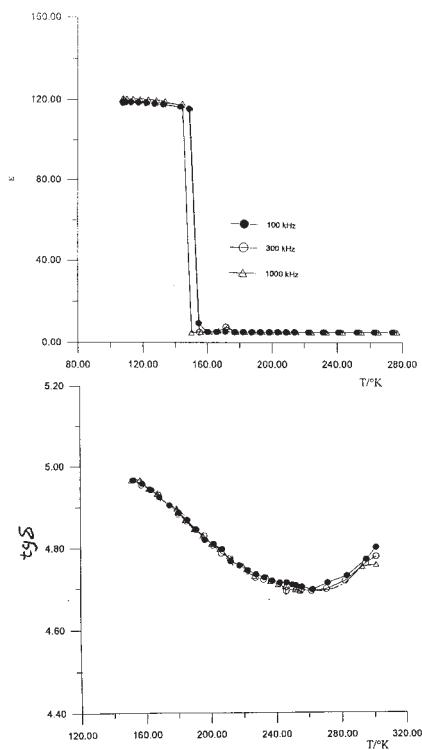
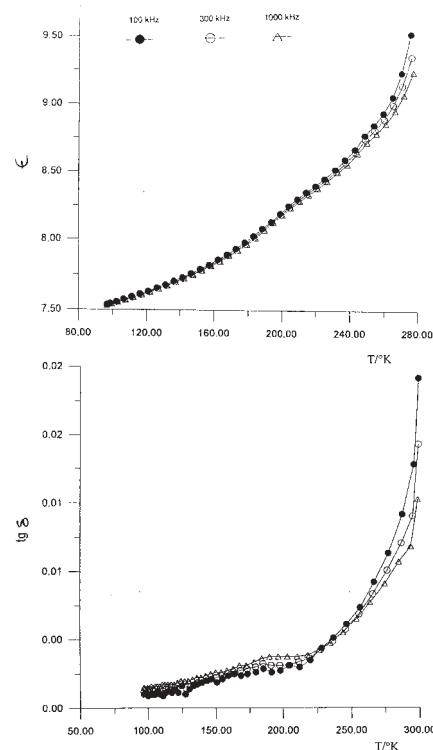Fig. 3. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Td* [Cd(DEA)SO$_4$] complex.

Fig. 4. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Oh* [Cd(DEA)$_2$SO$_4$] complex.

In conclusion, the position of the metals in the periodic table plays a major role in controlling their behaviour. The gradual change from 4d to 5d (*i.e.*, from Cd to Hg) results in the stepwise decrease of the permittivity and dielectric loss values.

The temperature dependence of τ can be expressed for thermally activated processes as:[28] $\tau = \tau_0 \exp(E_0/RT)$, where τ_0 is a constant characteristic relaxation time and represents the time of a single oscillation of a dipole in a potential well. E_0 is the energy of activation of the relaxation of a dipole and represents the average or most probable value of a spread of relaxation time.

From the analysis of the dielectric data of Cd-, and Hg-amino alcohol complexes, the relationships between the different dielectric parameters are obtained and are given in Table II.

By comparing the dielectric properties of the *Oh* [Zn(MEA)$_2$Cl$_2$][27] and *Oh* [Hg(MEA)$_2$Cl$_2$] complexes, the effect of changing the central metal ion on both ε and tg δ can be seen. In both complexes the relative permittivity values increase with increasing temperature. The relative permittivity value ranges were found to be 12 – 24 and 4 – 8 and the tg δ ranges were 0 – 0.4 and 0 – 0.15 for the *Oh* [Zn(MEA)$_2$Cl$_2$] and *Oh* [Hg(MEA)$_2$Cl$_2$] complexes, respectively. On the other hand, changing the central metal ion from 3d to 5d, the relative permittivity and the dielectric loss values decrease. The data are fairly in harmony with the physical properties of the metal, especially from its electronic structure.

TABLE II. Dielectric parameters obtained from the analysis of Cole-Cole diagrams for the cadmium and mercury amino alcohol complexes.

T	U	V	ϕ	α	f	ι_0	ε_0	ε_{00}	ι
Td [Cd(MEA)SO$_4$]									
210	4.7	2	28	24.2	100	6E+05	13	10.5	6E+05
220	3.6	2	48	30.57	500	11280	18.5	11	9756
230	3.5	2.7	41	26.11	100	1.078	28	11	0.86
240	4	3.3	50.51	32.17	200	0.32	28	12	0.259
250	4.6	3.5	36	22.93	200	0.319	47	5	0.224
260	3.3	2.5	33.5	21.34	500	0.09	26.5	12.5	0.074
280	7.5	1.4	9	5.732	500	0.897	31	14	0.733
290	7.7	1.6	2.073	1.32	500	5E-04	414	100	4E-04
300	7.7	2	0	0	500	8e-05	50.22	19.35	7E-05
ΔE = 15.7 kJ/mol									
Oh [Cd(MEA)$_2$SO$_4$]									
300	5	2	23	14.65	100	430.3	5.51	5.05	418.3
280	2.5	4	31	19.75	13000	2E-09	5.85	5.3	2E-09
270	4	4	30	19.11	13000	1E-05	5.86	5.31	1E-05
260	3.5	4	33	21.02	13000	8E-07	5.825	5.3	8E-07
250	3.5	3.8	34	21.66	130000	2E-06	5.835	5.23	2E-06
240	3.4	3.6	35	22.29	13000	4E-06	5.832	5.33	4E-06
230	3.5	4	34	21.66	13000	8E-07	5.825	5.3	8E-07
220	3.5	3.8	34	21.66	13000	2E-06	5.85	5.3	2E-06
210	5.2	3	29	18.47	12000	0.198	5.89	5.31	0.191
ΔE = 14.1 kJ/mol									
Td [Cd(DEA)SO$_4$]									
160	4.6	2.5	34	10.83	12000	0.005	5.77	5.375	0.005
170	2.5	1.5	54	17.2	5000	0.125	0.326	0.12	0.099
180	2.8	1.3	50	10.33	5000	0.041	0.306	0.12	0.033
190	2.5	1.3	55	17.52	5000	1.561	0.267	0.036	1.112
200	1.7	2	54	17.2	11000	1E-06	0.864	0.304	8E-07
210	1.4	2.5	16	5.096	12000	1E-06	0.128	0.144	1E-06
220	2.5	1.5	55	17.52	8000	0.092	9.4	1.875	0.067
230	2	2.5	50	15.92	11000	5E-07	0.752	0.1	4E-07
240	3.5	2	20	6.369	11000	3E-04	2.118	0.706	2E-04
280	4	3	37	11.78	35096	1E-04	1.854	0.417	7E-05
ΔE = 8.8 kJ/mol									

TABLE II. Continued

T	U	V	ϕ	α	f	ι_0	ε_0	ε_{00}	ι
Oh [Cd(DEA)$_2$SO$_4$]									
210	4.7	2	38	24.2	100	6E+05	13	10.5	6E+05
300	4.6	2	39	24.84	3000	22325	317	117	17630
290	4.1	2.9	40	25.48	3000	0.255	250	98	0.203
270	3.1	2.4	48	30.57	3000	0.103	175	78	0.084
250	2.6	1.7	57	36.31	500	1042	265	66	781.1
240	3.1	1.7	54	34.39	200	4E+05	290	70	3E+05
230	3.1	2	53	33.76	300	911.6	91	43	751.3
220	3	2.2	52	33.12	200	16.89	122	50	13.57
210	4.4	2.2	41	26.11	200	28925	230	50	21379
200	3.5	2.2	50	31.85	700	377.7	55	30	320.5
190	2	2.5	57	36.31	300	2E-07	43	27.3	2E-07
ΔE = 9.6 kJ/mol									
Td [Cd(TEA)SO$_4$]									
300	2.5	2	50	31.85	7000	0.022	9.33	8.617	0.022
290	3.2	1.8	25	15.92	7000	0.122	9.77	9.1	0.119
280	2.5	2.6	43	27.39	8000	7E-06	9.8	9.15	7E-06
260	2	2.8	45	28.66	8000	2E-09	9.9	9.3	2E-09
250	2	2.1	35	22.29	10000	6E-06	10.9	9.323	5E-06
240	3.6	3.6	34	21.66	13000	1E-05	10.07	9.47	1E-05
230	3.3	3.3	42	26.75	13000	1E-05	10.7	9.85	1E-05
220	3.8	3.4	38	24.2	13000	2E-04	10.63	9.7	2E-04
210	3.7	3.4	39	24.84	13000	9E-05	10.6	9.7	9E-05
200	4.1	3.3	33	21.02	13000	9E-04	10.8	9.8	9E-04
190	4	3.4	35	22.29	13000	4E-04	10.7	9.7	4E-04
160	5.3	3.6	31	19.75	12000	0.019	10.4	9.47	0.018
ΔE = 10.8 kJ/mol									
Oh [Cd(TEA)$_2$SO$_4$]									
300	4.6	2.3	20	12.74	3000	0.181	15.27	13.1	0.173
290	3	3.5	40	25.48	7000	5E-07	14.7	12.5	5E-07
280	7.3	3.5	0	0	2000	4E-05	15.3	11.5	4E-05
270	3.6	3.8	20	12.74	13000	6E-06	13.65	10.5	6E-06
260	6.5	3.5	10	6.369	12000	4E-04	13.1	10	3E-04
250	2.8	2.7	23	14.65	11000	2E-05	12.45	9.65	2E-05
240	3.5	3.8	23	14.65	13000	4E-06	11.35	9.75	4E-06
230	6.4	3.4	15	9.554	10000	0.004	11.5	9.2	0.003

TABLE II. Continued

T	U	V	ϕ	α	f	ιo	εo	εoo	ι
220	4.4	3.4	9	5.732	13000	4E-05	10.8	9.6	4E-05
210	4.3	5	20	12.74	1000	3E-05	10.35	9.1	3E-05
200	5.7	4.5	11	7.006	12000	5E-05	11.15	9.75	5E-05
130	5.7	4	14	8.917	13000	2E-04	10.48	9.2	2E-04

$\Delta E = 23.9$ kJ/mol

Oh [Hg(MEA)$_2$Cl$_2$]

T	U	V	ϕ	α	f	ιo	εo	εoo	ι
300	4.3	4	27	17.2	13000	4E-05	18.8	12.6	4E-05
290	6	4	8	5.096	6E-05	18.2	12.9	6E-05	
280	6	3	19	12.1	3000	0.117	15.8	12.6	0.109
270	6.4	3	14	8.917	100	0.642	15.15	12.36	0.602
260	7	2.2	10	6.369	100	0.796	15.3	12.35	0.745
250	6	3.5	12	7.643	100	0.057	14.45	12.25	0.054
240	1.6	4	40	25.48	11000	3E-15	14.2	12.7	3E-15
230	1.4	2.5	47	29.94	5000	2E-12	14.7	13.55	2E-12
220	5.2	3	26	16.56	13000	0.064	16	14	0.061
210	3	3.5	26	16.56	12000	1E-06	15.1	13.5	1E-06

$\Delta E = 13.9$ kJ/mol

Oh [Hg(DEA)$_2$Cl$_2$]

T	U	V	ϕ	α	f	ιo	εo	εoo	ι
190	6	3.3	15	9.554	11000	0.002	11.95	10.1	0.002
200	6	3.4	19	12.1	11000	0.008	12.1	10.2	0.008
210	7	2.5	11	7.006	11000	0.007	12.2	10.4	0.007
230	4.5	3.5	31	19.75	13000	0.001	11.95	10.4	0.001
240	5.5	5.5	22	14.01	12000	1E-05	12.29	10.45	1E-05
260	4.5	3	33	21.02	12000	0.044	12.9	10.35	0.042
280	4.7	2.7	34	21.66	2000	7.475	17.5	10	6.407
290	3.5	3	42	26.75	500	0.017	15.7	10	0.015
300	4.5	4.4	22	14.01	70	0.003	29	14.4	0.003

$\Delta E = 9.7$ kJ/mol

A similar trend was observed by comparing the dielectric behaviour of the *Oh* [Zn(MEA)$_2$SO$_4$] and *Oh* [Cd(MEA)$_2$SO$_4$] complexes.

Methods of calculations

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 $(\varepsilon_0 \pm \varepsilon_\infty)/2$.[28]

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.[28]
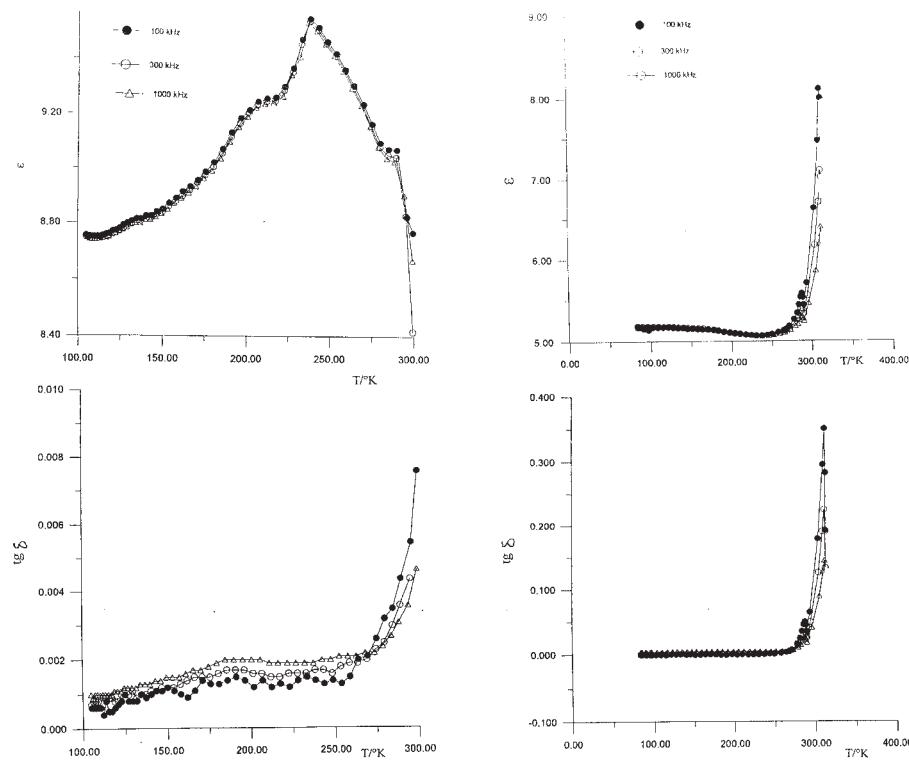
Fig. 5. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Td* [Cd(TEA)SO$_4$] complex.

Fig. 6. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Oh* [Cd(TEA)$_2$SO$_4$] complex.

The dielectric loss, tg δ, value depends on various external factors. The behaviour 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 tg δ at the phase transition temperature.

The familiar dielectric function, ε, may be expressed in terms of: $\varepsilon = \varepsilon' - i\varepsilon''$ ($i = \sqrt{-1}$, ε' and ε'' have both been defined before).

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.[28,29] Knowing α, τ_0 can be determined using the relation: $U/V = (\omega\tau_0)^{1-\alpha}$. 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, $\omega = 2\pi\nu$. 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.[29] The molecular relaxation
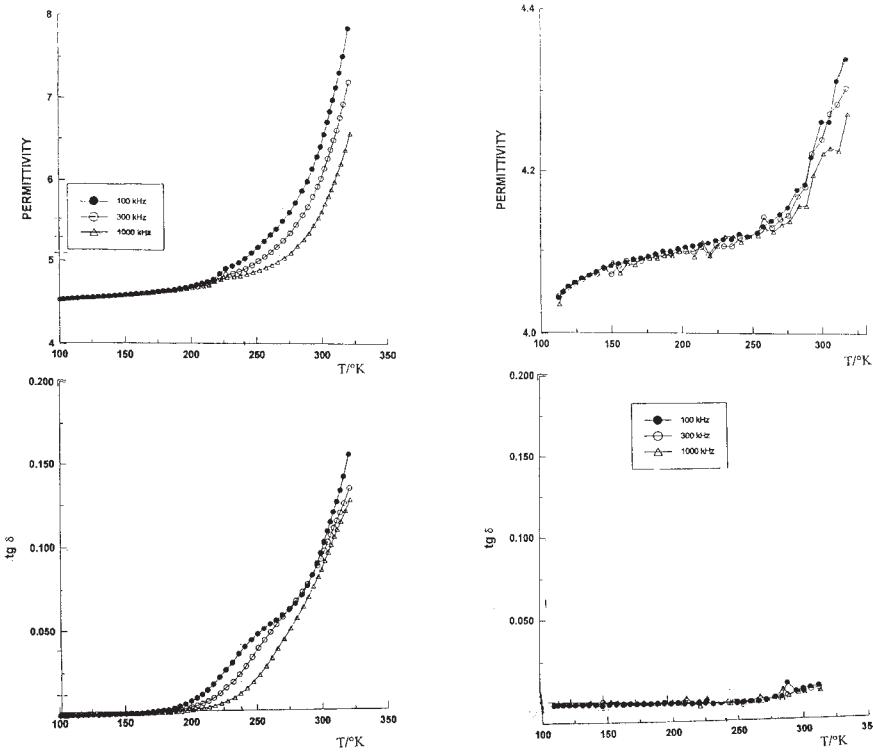
Fig. 7. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Oh* [Hg(MEA)$_2$Cl$_2$] complex.

Fig. 8. Permittivity and dielectric loss dependence on temperature at different frequencies for the *Oh* [Hg(DEA)$_2$Cl$_2$] complex.

time τ could be determined based on the following equation:[29]

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

The temperature dependence of τ can be expressed by a thermally activated process in the frame of an Arrhenius concept of the type:[30,31] $\tau = \tau_0 \exp(-E_0/kT)$, 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 is the energy of activation for the relaxation of the dipole, τ represents the average or most probable value of the spread of the relaxation times.

In conclusion, the relative permittivity and dielectric loss values for the amino alcohol complexes indicate a dipolar mechanism of polarization.

The data reveals semi-conducting features based mainly on the hopping mechanism.

ИЗВОД

ДИЕЛЕКТРИЧНЕ ОСОБИНЕ НЕКИХ КОМПЛЕКСА КАДМИЈУМА И ЖИВЕ СА АМИНО–АЛКОХОЛИМА НА НИСКИМ ТЕМПЕРАТУРЕАМА

MAMDOUH S. MASOUD[a], AHMED M. HAFEZ[b], M. SH. RAMADAN[a] and ALAA E. ALI[c]

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

Проучаване су диелектричне особине неких комплекса кадмијума и живе са амино-алкохолима у области температуре 100 – 300 K и на фреквванцијама од 100, 300 и 1000 Hz. Предложени су механизми поларизације, а анализиране су и зависности и ε и tg δ од температуре и фреквенције. Анализа података указује на полупроводничке особине одређене првенствено механизмом прескока.

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