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Dielectric Behaviour of Metal Complexes Cu (II), Ni (II) and UO₂ (VI) Of the Ligand Oxaloanilic Acid Hydrazone

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Abstract: The dielectric behaviour and molecular structure of metal complexes Cu(II), Ni(II) and UO₂(VI) of the ligand oxaloanilic acid hydrazone have been investigated using Time Domain Reflectometry (TDR) technique in the frequency range 10 MHz to 10GHz. Cole-Davidson model has been applied for fitting the complex permittivity spectra [$\epsilon^*(\omega)$]. The parameters ϵ_s –the static permittivity, τ - the dielectric relaxation time are evaluated at different temperatures from 288⁰K to 333⁰K and are discussed in respect of their molecular structural behaviours. The thermodynamic parameters, such as ΔH^* - molar enthalpy, ΔS^* - the molar entropy are obtained using Eyring's rate equation. In the light of such data the possible structures of the present complexes are discussed.

Keywords: Dielectric , Time Domain Reflectometry

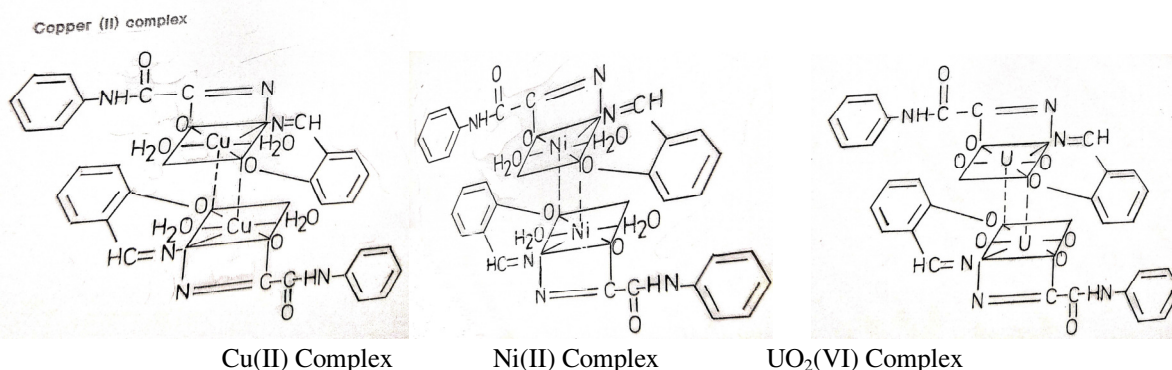
I. INTRODUCTION

The knowledge of dielectric relaxation and static permittivity leads to understanding of the geometrical changes within the molecules. Hence, by knowing indirectly interfacial polarization, counterion moments and spatial changes in the domain size[1] of the molecules, it would be possible to speak of the structural behavior of the molecules.

The authors have undertaken the experimental study of evaluating dielectric parameters with the present metal complexes of ligand oxaloanilic acid hydrazone belonging to azo methane group chelates [2,3] under Time Domain Reflectometry (TDR) described elsewhere [4,5]. In addition, for understanding more of the dielectric behavior of the complexes, the required dipole moments have been evaluated in conjunction with which the structures [6,7] are discussed.

II. EXPERIMENTAL

The metal complexes were prepared by using the methods reported elsewhere[8]. The prepared compounds were crystallized repetitively from ethanol for purity and the same were checked by elemental analysis. The solution was prepared with commercially available DMSO of 99% pure EMARCK BDH AR reagents grade chemicals were used grade, just before recording the TDR spectra. Mixtures of various compositions were done by appropriate weight fraction of the complexes weighed in Zurich- Mettler balance at room temperature (300±1⁰K).



A Tektronix 7854 sampling oscilloscope with 7512 TDR unit has been used. The sample was placed in the standard military application cell (SMA) of 3.5mm and 1.52mm outer and inner diameters respectively, having the pin length 1.28mm. Its effective pin length due to fringing effect of the field was found to be 1.35mm. A time window of 5 ns was used for all such measurements. The records of permittivity spectra were obtained by using bilinear calibration method.

In TDR the pulse reflected from cell without sample $R_1(t)$ is compared with pulse reflected from the cell with the sample $R_s(t)$. These two pulses were digitized with 1024 sampling points in the selected time window of 5 ns. The two pulses are subtracted and added in the oscilloscope memory and are transferred to PC/XT, via GPIB to Fourier Transform and data processing. The permittivity spectra $\epsilon^*(\omega) = \epsilon' - j\epsilon''$ were determined by using bilinear calibration method [9]. The dielectric parameters have been fitted by Debye expression [10] using nonlinear least squares fit method.

Using standard experimental techniques, the measurement of refractive indices was carried out at optical frequency on a set of graded concentrations of the solute in the solvent DMSO at room temperature. Density measurements were done with the method described elsewhere.

III. RESULTS

The dielectric measurements were carried out as a function of temperature on a set of graded concentrations (weight fraction) of the metal complexes in DMSO, a non-associative polar liquid as solvent. The complex permittivity spectra $\epsilon^*(\omega)$ were fitted to Cole-Davidson equation using nonlinear least squares fit method as described elsewhere to obtain dielectric parameters.

The raw and corrected spectra of the complexes are represented graphically in figs1 (a) to 1(c). The evaluated parameters ϵ_s and τ for various compositions of mixtures at different temperatures are entered in Table 1-3. The calculated molar enthalpy of activation ΔH^*_E (Eyring) and ΔH^*_A (Arrhenius) and molar entropy ΔS^*_E (Eyring) and Gibb's Free energy of Activation ΔG^* are also entered in the same tables 1-3. The graphical representation of the variation of relaxation time (τ) versus concentration (C) and variation of Gibb's free energy of activation (ΔG^*) versus relaxation time (τ) as against concentration 1.0 gm/cc has been shown in figs.2(a) to 2(c) and 3(a) to 3(c) respectively. The refractive indices are given for various concentration in tables 1-3.

Dipole moments have been evaluated at room temperature using following equation, by taking parameter $h = 6.8$ with the calibrated μ of DMSO.

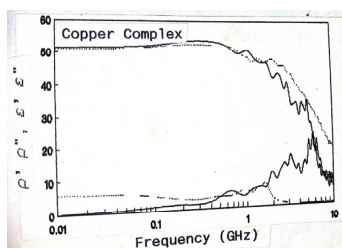


Figure1. a

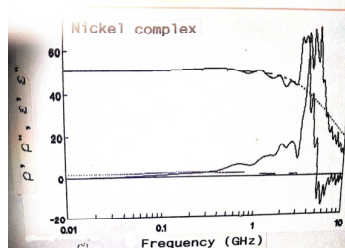


Figure1. b

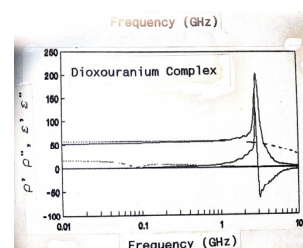


Figure1. c

Comparison between raw spectrum $\epsilon''(\omega)$ and corrected dielectric spectrum $\epsilon''(\omega)$ for complexes (0.25 mg/ml concentration) at 30⁰

$$\epsilon_0 - \epsilon_\infty \text{ (M/m)} = 4 \pi N h \mu^2 / 9kT$$

For calculating radius of the molecule, Debye expression has been used. These were calculated at different temperatures as against concentration 1.000/cc.

IV. DISCUSSION AND CONCLUSION

The electric dipole moment of metal complexes, namely Cu (II), Ni (II), and UO₂(VI) are emerged as 35.83D, 68.59 D and 98.3 D and Guggenheim 35.607, 67.734, 96.915 respectively. Although these values are large as compared to the values by using Guggenheim [5] equation, such large values are reported in the literature [11] for polymers, obtained in both polar and non polar solvents. These observed/calculated values of the dipole moments may be taken as indicative of the fact that the present complexes are associated values of dipole moment, in general which in turn may be as suggestive of having tetrahedral structure. Our XRD study on these complexes almost has confirmed this fact.

In the present investigation, observed relaxation time seem to vary for all the present metal complexes with the temperature for a particular concentration. From the tables 1-3, it is clear that the relaxation time decreases as the temperature increases which is in accordance with the Debye equation.

In view of the above facts, keeping $\tau = 24.6$ ps to be the relaxation time for DMSO at room temperature, it may be said that either the solute-solute interaction play a role in such a way as to make reorientation of the dipoles more easier or that the τ value of solute is shorter compared to that of solvent DMSO molecule. But, the latter case is hard to justify since the solute molecules are much heavier than the solvent DMSO molecule, thus expecting a large τ for the solute molecule. Hence, it can be said that the observed dielectric absorption may be due to both inter- as well as intra- molecular rotations i.e, it may be due to overall rotation of the molecule.

It is suggested in the literature that a benzene compound studied in benzene solution has a value of τ in the range of 8 to 16 ps [12,13]. Taking this as a crude guideline, one can expect at least about 32 ps in the case of present complexes as those contain four benzene rings in their configurations. As the observed values do not agree fully with expected ones this may be partly due to the fact that presently used solvent is a polar one. However, the authors feel that they are of the right order of magnitude.

From the tables 1-3, it is found that ΔH^\ddagger varies in accordance with the concentration. The negative values of ΔS^\ddagger in all concentrations may indicate a more ordered molecular state. As noted in the literature, ΔG^\ddagger , the Gibb's free energy of activation and τ , relaxation time are dependent on temperature. Hence when the temperature increases there should be increase in Gibb's free energy of activation, this makes the molecule oriented in a shorter time. As a result the relaxation time decreases, The same trend has been observed in the present complexes. The dielectric relaxation parameters for the present metal complexes have been determined at various temperatures by using the time domain reflectometry. For making these parameters more reliable, the method of calibration process based on the least squares fit has been used. As the solvent DMSO molecule is much smaller than the present solute molecule, it is very much difficult to pass a remark regarding the outcome of smaller values of relaxation time in the present findings. However, under the existing circumstances, it can be said that the observed dielectric absorption may be due to both inter- as well as intra- molecular rotations and as such the present result may be argued on the basis of taking into consideration the overall rotation of the molecule. Further, the mismatch of τ with the expected one (32 ps) may be due to the polar solvent DMSO molecule. In arguing these values, more stress has been put on their trend as they are found to be in right order of magnitude. Depending on the negative characteristics of ΔS^\ddagger . The molar entropy of activation, a more ordered molecular state has been emphasized. The dependence of the Gibb's free energy of activation, ΔG^\ddagger and relaxation time τ on the temperature has been established with the present findings

Table 1 .Variation of parameters of copper (II) complex

Conc Mg/ml	Temp °K	ε _s	T 10 ⁻¹²	ΔH _A [‡] KJmol ⁻¹	ΔH _E [‡] Jmol ⁻¹	ΔS _E [‡] Jmol ⁻¹	ΔG [‡] KJmol ⁻¹	RI n	μ Debye	μ Debye Guggen- heim	r 10 ¹⁰ radius of molecule				
0.0625	288	44.8(1)	24.5(9)	6.188	3.69 7	-168.92	52.360	1.487	35.83	35.67					
	303	46.5(2)	21.1(9)				54.895								
	318	45.4(1)	19.0(8)				57.429								
	333	43.9(2)	17.2(8)				59.964								
0.1250	288	45.2(0)	23.5(7)	5.587	2.98 1	-166.74	51.002	1.486			35.83	35.67			
	303	45.9(0)	22.8(7)				53.503								
	318	43.1(3)	18.0(2)				56.004								
	333	43.5(1)	17.9(9)				58.505								
0.2500	288	47.2(1)	24.8(9)	7.271	4.69 3	-172.04	54.240	1.4787					35.83	35.67	
	303	45.2(1)	23.1(9)				56.821								
	318	43.7(0)	18.8(6)				59.401								
	333	43.8(2)	16.8(7)				61.982								
0.5000	288	46.6(0)	23.6(6)	6.531	3.93 9	-169.86	60.502	1.4793	35.83	35.67					
	303	46.2(0)	22.6(7)				55.407								
	318	44.6(1)	17.7(6)				57.954								
	333	43.9(2)	17.0(1)				60.502								
0.1000	288	46.7(1)	23.4(9)	6.209	3.69 0	-169.24	52.431	1.4828			35.83	35.67			1.66
	303	45.3(1)	21.0(8)				54.970								1.62
	318	44.4(2)	17.9(8)				57.508								1.56
	333	41.6(3)	16.7(7)				60.047								1.55

Table 2. Variation of parameters of Nickel (II) complex

Conc Mg/ml	Temp °K	ϵ_s	T 10-12	ΔH_A^* KJ Mol ⁻¹	ΔH_E^* J Mol ⁻¹	ΔS_E^* J Mol ⁻¹	ΔG^* KJ Mol ⁻¹	RI n	μ Debye	μ Debye Guggenhei m	r 10 ¹⁰ radius of molecule				
0.0625	288	49.8(1)	29.4(9)	7.044	4.540	-171.40	53.615	1.480	68.59	67.734					
	303	47.4(1)	24.6(9)				56.171								
	318 333	44.4(3) 43.6(1)	20.9(3) 20.0(2)				58.727 61.283								
0.1250	288	47.8(1)	29.0(2)	6.027	3.412	-166.62	51.398	1.4808			68.59	67.734			
	303	48.5(1)	26.1(9)				53.897								
	318 333	44.1(2) 44.8(2)	20.3(2) 21.7(9)				56.397 58.895								
0.2500	288	48.9(2)	29.0(2)	6.132	3.600	-167.25	51.768	1.4804					68.59	67.734	
	303	48.2(1)	25.2(9)				54.277								
	318 333	45.6(2) 44.1(2)	21.9(2) 20.7(2)				56.785 59.294								
0.5000	288	47.8(2)	28.9(2)	6.070	3.467	-166.77	51.496	1.4806	68.59	67.734					
	303	48.4(1)	25.9(9)				53.998								
	318 333	50.1(4) 44.3(1)	21.4(2) 21.1(9)				56.500 59.001								
0.1000	288	46.9(2)	21.6(2)	8.930	3.732	-167.86	52.076	1.4801			68.59	67.734			1.78
	303	50.2(3)	23.6(2)				54.594								1.68
	318 333	43.3(2) 45.0(1)	20.9(2) 20.9(8)				57.111 59.629								1.64 1.66

Table 3 .Variation of parameters of DIOXOURANIUM (VI) compl

Conc Mg/ml	Temp °K	ε _s	T 10-12	ΔH _A [*] KJ Mol ⁻¹	ΔH _E [*] J Mol ⁻¹	ΔS _E [*] J Mol ⁻¹	ΔG [*] KJ Mol ⁻¹	RI N	μ Debye	μ Debye Guggenh eim	r 10 ¹⁰ radius of molecule				
0.0625	288	48.1(1)	29.0(2)	2.189	2.595	-163.51	49.688	1.4826	98.3	96.915					
	303	44.2(1)	26.4(8)				52.140								
	333	45.2(2)	23.6(9)				57.046								
0.1250	288	48.5(2)	27.6(2)	3.811	1.334	-159.30	47.212	1.4797			98.3	96.915			
	303	47.2(1)	28.1(2)				49.601								
	333	39.4(2)	23.7(2)				54.381								
0.2500	288	48.4(1)	28.1(10)	4.927	2.295	-162.80	49.181	1.4828					98.3	96.915	
	303	49.2(1)	26.1(1)				51.623								
	333	44.6(1)	23.2(1)				56.507								
0.5000	288	47.2(3)	27.5(2)	2.839	0.940	-158.42	46.565	1.4807	98.3	96.915					
	303	45.4(3)	25.6(2)				48.941								
	333	40.0(2)	24.6(1)				53.694								
0.1000	288	46.6(1)	29.5(1)	2.432	4.157	-168.98	52.247	1.4808			98.3	96.915			1.76
	303	47.5(1)	25.7(9)				54.752								1.72
	333	43.3(1)	25.5(1)				60.427								1.69

Variation of relaxation time with concentration of complexes

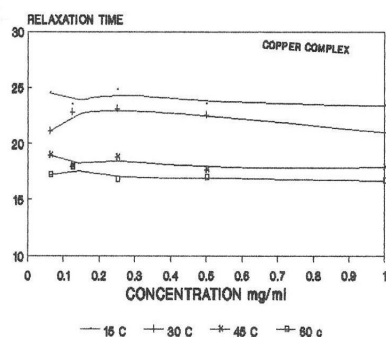


Figure 2 a

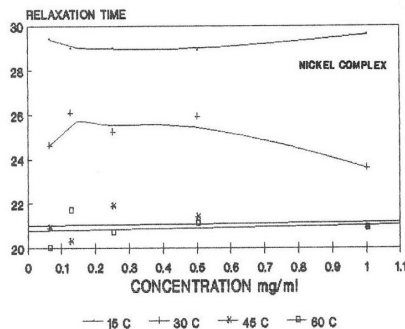


Figure 2 b

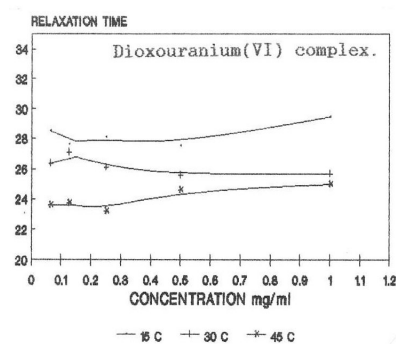


Figure 2 c

Variation of Activation of energy with relaxation of complexes

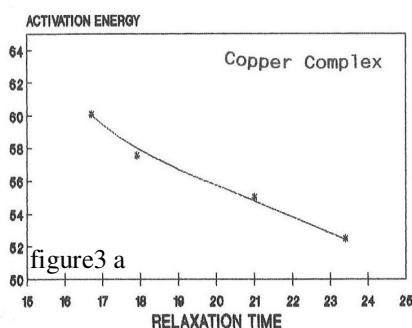


figure3 a

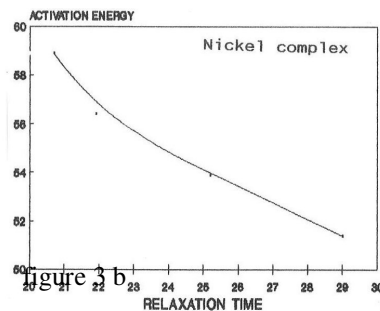


figure 3 b

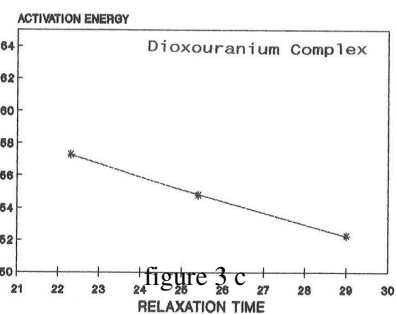


figure 3 c

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