12. Adachi, H.; Mitsuyu, T.; Yamazaki, O.; Wasa, K. *J. Appl. Phys.* **1986**, *60*, 736.

13. Castellano, R. N.; Feinstein, L. G. *J. Appl. Phys.* **1979**, *50*, 4406.

14. Oikawa, M.; Toda, K. *Appl. Phys. Lett.* **1976**, *29*, 491.

15. Leonard, A.; Suzuki, S.; Fripiat, J. J.; Dekimpe, C. *J. Phys. Chem.* **1964**, *68*, 2608.

16. Aelion, R.; Loebel, A.; Eirich, F. *J. Amer. Chem. Soc.* **1950**, *72*, 5705.

17. Peace, B. W.; Mayhan, K. G.; Montle, J. F. *Polymer* **1973**, *14*, 420.

18. Choy, J. H.; Han, Y. S.; Kim, J. T. *J. Mater. Chem.* **1995**, *5*, 65.

19. Bradley, D. C.; Wardlaw, W. *J. Chem. Soc.* **1951**, *73*, 280.

20. Bradley, D. C.; Mehrota, R. C.; Swanwick, J. D.; Wardlaw, W. *J. Chem. Soc.* **1953**, *73*, 2025.

21. Martin, R. L.; Winter, G. *J. Chem. Soc.* **1961**, 2947.

22. Kolb, U.; Abraham, I.; Gutwerk, D.; Ertel, T. S.; Hörner, W.; Bertagnolli, H.; Merklein, S.; Sporn, D. *Physica B* **1995**, *208-209*, 601.

23. Li, S.; Condrate sr, R. A.; Jang, S. D.; Spriggs, R. M. *J. Mater Sci.* **1989**, *24*, 3873.

24. Oh, Y. J.; Jung, H. J. *J. Kor. Ceram. Soc.* **1991**, *28*, 943.

25. Calzada, M. L.; Olmo, L. D. *J. Non-Crystall. Sol.* **1990**, *121*, 413.

26. Yoldas, B. E. *J. Non-Crystall. Sol.* **1982**, *51*, 105.

27. Sakka, S.; Kamiya, K. *J. Non-Crystall. Sol.* **1982**, *48*, 31.

28. Fukushima, J.; Kodaira, K.; Matsushita, T. *J. Mater Sci.* **1984**, *19*, 595.

29. Hong, S. T.; Lim, J. T.; Lee, J. C.; Xue, M.; Lee, I. M. *Bull. Kor. Chem. Soc.* **1996**, *17*, 637.

30. Takahashi, Y.; Yamaguchi, K. *J. Mater Sci.* **1990**, *25*, 3950.

31. Francis, L. F.; Oh, Y. J.; Payne, D. A. *J. Mater Sci.* **1990**, *25*, 5007.

Thermo-Physical Properties of Some Coumarin Complexes

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A number of complexes of transition metal ions with some coumarin derivatives have been prepared and their structures were elucidated with the help of conductometric, photometric and infrared studies. The stability constants of various complexes were determined, in aqueous medium, at different temperatures potentiometrically. The thermodynamic characteristics, ΔG, ΔH and ΔS, were calculated. The electrical behaviour of prepared compounds was followed.

Introduction

An increased interest in coumarin chemistry is mainly due to a wide spectrum of their biological activities. The coumarin skeleton is related to many natural products, *e.g.*, the Umbelliferae and Rutaceae families, and drugs, *e.g.* antifungi, carcinogenics and anticoagulatives. Consequently, synthesis and reactivity of coumarins have been extensively studied.[1-4] The structures were established by spectroscopical techniques.

As a part of the ongoing interest in the area of physical properties of complexes, a number of some substituted coumarins were complexed with different transition metal ions and their thermodynamic characteristics were studied. Potentiometric, conductometric, photometric and spectral techniques were used in this work. The electrical conductivity of solid samples was also investigated.

Experimental

All the chemicals used were of AR grade. Details of the preparation of coumarin derivatives used in the present study are the same as reported previously.[5-8] The prepared coumarins have the following structures:
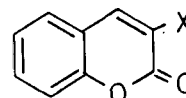
Ligand I : X=NH$_2$ Ligand III : X=CN
Ligand II : X=OH   Ligand IV : X=COOC$_2$H$_5$

All potentiometric measurements were made with a digital pH-meter 5800-05 solution analyzer, Cole Parmer, with a glass calomel electrode assembly. Solutions of the different ligands were prepared in hot ethanol. Three titrations, *viz.* titration of a) free hydrochloric acid, b) free acid plus coumarin, and c) free acid plus coumarin plus the metal ion, were carried out in aqueous medium against 0.01 M KOH at 298, 313 and 323 K, respectively. Initial ionic strength of all the solutions was maintained at 0.1 M by adding requisite amounts of KCl. The stability constants were calculated according to the Irving and Rossotti's method.[9]

The thermodynamic parameters ΔG, ΔH and ΔS of the coumarin complexes were evaluated from the stability constant values,[10] where $\Delta G = -2.303\, RT \log K$. The enthalpy and entropy changes were obtained using the relations:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

and $\quad \Delta G = \Delta H - T\,\Delta S$

In order to understand the nature of the complex formation process, the conventional thermodynamic functions were analyzed into electrostatic and non-electrostatic terms[11]:

$$\Delta G = \Delta G_{non} + \Delta G_{el} = nRT \ln M + RC(a + e^{T/\theta})$$

$$\Delta H = \Delta H_{non} + \Delta H_{el} = RC\left[a + (1 - \frac{T}{\theta})e^{T/\theta}\right]$$

$$\Delta S = \Delta S_{non} + \Delta S_{el} = -nR \ln M - \frac{RC}{\theta}e^{T/\theta}$$

θ is the temperature characteristic of the solvent and M is its molality. The values of the parameters C and a are used to determine the separated thermodynamic functions.

To demonstrate the stoichiometric ratio of complexes, conductometric and photometric titration techniques were used at room temperature.[12] The conductograms were obtained by titrating 30 mL of 10^{-3} M of $CuCl_2$ solution, as a representative salt solution, against 10^{-2} M of various solutions of coumarins using a digital conductivity meter 5800-05 solution analyzer. Photometric titration curves were followed by aid of Milton Roy, Spectronic 1201, under fixed concentration of metal cations $(1.0 \times 10^{-4}$ M) with different concentrations of coumarin solutions $(0.5 \times 10^{-4}\text{-}3.5 \times 10^{-4}$ M).

Solid complexes of molar ratio 1:2 (metal:coumarin) were prepared by refluxing ethanolic solution of coumarin with corresponding metal chlorides for 3 h., then cooled. The complexes obtained were filtered and washed repeatedly with ethanol to remove excess of coumarin. The structure of complexes was characterized using a Shimadzu IR-440 spectrophotometer.

The electrical conductivity measurements of solid samples were carried out on discs of 13 mm diameter and 0.6-0.8 mm thickness in the temperature range 298-430 K. The samples were pressed under a pressure of 5 ton/cm² in a hydraulic press set. The two point probe technique was used by help of a Ni/Ni-Cr thermocouple.[13] A fixed voltage of 10 V was applied. The conductivity values of the samples were obtained during the cooling process to exclude the effect of moisture or adsorbed water vapour.

Results and Discussion

From the potentiometric titration curves, the proton-ligand, pK, and metal-ligand, log K, constants are determined using the standard expressions.[14] The values of stability constants are given in Table 1. The results show that more than one coumarin complex will be present in a given solution, and thus two successive stability constants, log K_1 and log K_2, are obtained. This may be attributed to the formation of M : L and M:2L complexes. For statistical, electrostatic and steric reasons, the values of these constants are always decreased in the order: $K_1 > K_2 \cdots$ etc.[15] By combining these

Table 1. Stability constants and thermodynamic data of coumarin complexes at 298 K

Compounds	log K	$-\Delta G$ (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.deg.)
Ligand I (aminocoumarin)				
Mn complex	5.52	31.50	−51.60	−67.45
	(4.00)	(22.82)	(−49.76)	(−90.40)
Fe complex	5.72	32.64	−44.23	−38.89
	(5.16)	(29.44)	(−33.17)	(−12.52)
Co complex	6.20	35.38	−66.35	−103.9
	(5.20)	(29.67)	(−47.92)	(−61.24)
Ni complex	6.40	36.52	−58.98	−75.37
	(5.36)	(30.58)	(−47.92)	(−58.19)
Cu complex	6.48	36.97	−73.72	−123.3
	(5.04)	(28.76)	(−55.29)	(−89.03)
Ligand II (hydroxycoumarin)				
Mn complex	3.42	19.51	53.08	243.58
	(3.19)	(18.20)	(50.87)	(231.77)
Fe complex	3.92	22.37	60.45	277.92
	(3.58)	(20.43)	(37.60)	(194.72)
Co complex	3.87	22.08	35.39	192.84
	(3.28)	(18.72)	(38.29)	(191.31)
Ni complex	3.94	22.48	40.55	211.50
	(3.75)	(21.40)	(42.12)	(213.15)
Cu complex	4.13	23.57	61.92	286.89
	(3.89)	(22.20)	(53.61)	(254.40)
Ligand III (cyanocoumarin)				
Mn complex	5.04	28.76	−55.29	−89.03
	(4.74)	(27.05)	(−38.33)	(−37.87)
Fe complex	5.56	31.72	−47.92	−54.35
	(4.80)	(27.39)	(−44.23)	(−56.51)
Co complex	5.72	32.64	−58.98	−88.37
	(4.80)	(27.39)	(−53.61)	(−87.99)
Ni complex	6.08	34.69	−76.59	−140.6
	(4.96)	(28.30)	(−53.61)	(−84.93)
Cu complex	6.76	38.57	−84.78	−155.1
	(4.88)	(27.84)	(−55.29)	(−92.11)
Ligand IV (ethyl coumarincarboxylate)				
Mn complex	3.72	21.23	−19.15	6.98
	(3.40)	(19.40)	(−11.06)	(27.99)
Fe complex	5.04	28.76	−18.43	34.66
	(3.64)	(20.77)	(−11.06)	(32.59)
Co complex	4.48	25.56	−23.59	6.61
	(3.64)	(20.77)	(−11.06)	(32.59)
Ni complex	4.56	26.02	−22.12	13.10
	(3.84)	(21.91)	(−11.49)	(34.97)
Cu complex	5.00	28.53	−14.74	46.26
	(4.32)	(24.65)	(−13.40)	(37.75)

Values in parantheses are for reactions involving formation of 1 : 2 complexes.

values, the overall stability constants are obtained. Generally, the trend of increasing stability of the various coumarin complexes follows the Irving-Williams order,[15] *i.e.*, Mn < Fe < Co < Ni < Cu.

A comparison of the stabilities of coumarins-metal com-

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plexes was undertaken in order to evaluate the effect of different substituents present on the coumarin ring on the formation of complexes. It is apparent that the trend of increasing stability is: I > III > IV > II. The complexing tendency of the substituents is in a good agreement with the expectance of spectrochemical series.[16] On the other hand, the stability constants of coumarin I, III and IV complexes decrease with rising of the temperature suggesting an exothermic nature of the interaction. An endothermic nature is observed for the formation of coumarin II complex. However, all coumarin complexes have negative values of ΔG indicating that the formation of complexes is a spontaneous process and thermodynamically stable. These conclusions are ascertained by the data of the enthalpy change, where negative values are obtained for the formation of complexes with coumarins I, III and IV, but positive values are obtained for coumarin II complexes.

The heat of formation of a complex is the enthalpy evolved or absorbed during the formation reaction. The greater the heat evolution in the reaction, the lower the final potential energy is expected to be and so the more stable the final product.[17] Consequently, i) the more negative the value of ΔH becomes the more stable is the system, ii) the more positive the value of ΔS (the greater the disorder), the more stable is the system. In view of the heat of formation, the stability of complexes takes the trend: III > I > IV > II.

For amino- and cyanocoumarin complexes (I and III), the complexing processes are accompanied by decreasing of entropy. The increase of entropy during the formation of hydroxy- and ethyl-coumarincarboxylate (II and IV) are attributed to an increase in the disorder of these complexes. Therefore, from the thermodynamic point of view, probably, the best complexing agent is ethyl-coumarincarboxylate which possesses negative ΔH values and positive ΔS values.

To illustrate the nature of the chemical bonding of coumarin complexes, the thermodynamic data are divided into two parts, *i.e.*, electrostatic and non-electrostatic, as summarized in Table 2. It is obvious that ΔG_{non} values are more negative than ΔG_{el} values for the metal complexes of coumarins I and III indicating that non-electrostatic forces are stronger than electrostatic forces. Conversly, the formation of complexes with coumarins II and IV, *i.e.*, the electrostatic are stronger than the non-electrostatic forces.

The ΔH_{non} values reflect the covalency of the bonding and structural changes on the complex formation process. The covalency nature of the different coumarins complexes decreases in the direction: cyano-, amino-, ethylcarboxylate, hydroxycoumarin complexes.

Conductometric titration method is a physical chemical measurement that provides information about the composition of complexes in a given solution. The variation of the conductance of copper chloride solution during the addition of the corresponding coumarin derivative was followed. The conductograms are represented in Figure 1. The point of inflection in the conductograms illustrates the composition of complexes.[18] It is clear that the various coumarins form stable complexes with a molar ratio 1 : 2 (metal : coumarin).

Photometric titration method is particularly valuable for studying the composition of complexes.[19] The concentration of metal ion is kept fixed and that of corresponding cou-

Table 2. Electrostatic and non-electrostatic components of thermodynamic parameters of coumarin complexes at 298 K

Compounds	ΔG_{non}	ΔG_{el}	ΔH_{non}	ΔH_{el}	ΔS_{el}
Ligand I					
Mn complex	– 38.96	7.46	– 48.91	– 2.69	– 34.06
	(– 27.99)	(5.17)	(– 47.89)	(– 1.87)	(– 23.62)
Fe complex	– 33.84	1.20	– 43.80	– 0.43	– 5.50
	(– 13.90)	(– 1.76)	(– 33.80)	(0.63)	(8.03)
Co complex	– 50.83	15.45	– 60.78	– 5.57	– 70.54
	(– 28.46)	(– 1.21)	(– 48.36)	(0.44)	(5.54)
Ni complex	– 45.71	9.19	– 55.66	– 3.32	– 41.98
	(– 28.70)	(– 1.88)	(– 48.60)	(0.68)	(8.59)
Cu complex	– 59.30	12.38	– 69.25	– 4.47	– 56.54
	(– 33.63)	(4.87)	(– 53.53)	(– 1.76)	(– 22.25)
Ligand II					
Mn complex	41.15	– 60.66	31.20	21.88	276.97
	(47.19)	(– 65.38)	(27.28)	(23.59)	(298.55)
Fe complex	45.81	– 68.18	35.86	24.59	311.31
	(36.84)	(– 57.27)	(16.94)	(20.66)	(261.50)
Co complex	27.47	– 49.54	17.52	17.87	226.23
	(37.80)	(– 56.52)	(17.90)	(20.39)	(258.09)
Ni complex	31.15	– 53.63	21.20	19.35	244.89
	(39.91)	(– 61.31)	(20.01)	(22.11)	(279.93)
Cu complex	46.57	– 70.14	36.62	25.30	320.28
	(48.14)	(– 70.34)	(28.24)	(25.37)	(321.18)
Ligand III					
Mn Complex	– 40.94	12.18	– 50.89	– 4.40	– 55.64
	(– 20.71)	(– 6.33)	(– 40.61)	(2.28)	(28.91)
Fe complex	– 36.31	4.59	– 46.26	– 1.66	– 20.96
	(– 25.14)	(– 2.25)	(– 45.04)	(0.81)	(10.27)
Co complex	– 44.69	12.04	– 54.64	– 4.34	– 54.98
	(– 32.03)	(4.64)	(– 51.93)	(– 1.68)	(– 21.21)
Ni complex	– 58.17	23.48	– 68.12	– 8.47	107.21
	(– 32.27)	(3.97)	(– 52.18)	(– 1.43)	(– 18.15)
Cu complex	– 65.22	26.65	– 75.17	– 9.61	– 121.67
	(– 33.39)	(5.55)	(– 53.29)	(– 2.00)	(– 25.33)
Ligand IV					
Mn complex	– 12.39	– 8.84	– 22.34	3.19	40.37
	(1.35)	(– 20.76)	(– 18.55)	(7.49)	(94.77)
Fe complex	– 13.86	– 14.90	– 23.81	5.38	68.05
	(0.99)	(– 21.76)	(– 18.91)	(7.85)	(99.37)
Co complex	– 16.80	– 8.76	– 26.75	3.16	40.00
	(0.99)	(– 21.76)	(– 18.91)	(7.85)	(99.37)
Ni complex	– 15.84	– 10.18	25.79	3.67	47.49
	(0.37)	(– 22.28)	(– 19.53)	(8.04)	(101.75)
Cu complex	– 11.08	– 17.44	– 21.03	6.29	79.65
	(– 1.76)	(– 22.89)	(– 21.66)	(8.26)	(104.53)

marin varied to give a series of [L]/[M] ratios. The absorbances of these solutions, measured at an absorption maximum for the complex, increase linearly up to the molar ratio of the complex, at which virtually the whole amount of both components is complexed.

Further addition of coumarin can not increase the absorbance and thus the line becomes horizontal. The maximum absorption band of free aminocoumarin was found at 303 nm while after complexation this band was shifted to
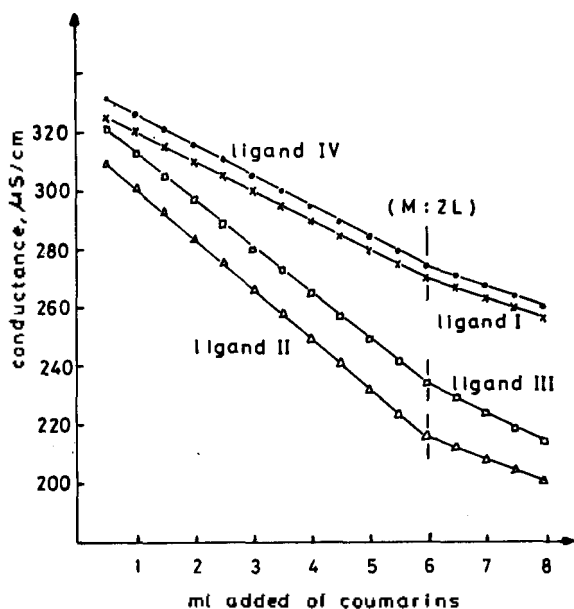
Figure 1. Conductometric titration curves of coumarins with copper ions.

312-318 nm. On the other side, the maximum absorption band of hydroxycoumarin was observed at 322 nm and its complexes in the range 308-318 nm. The photometric data indicate that the different coumarins form stable complexes with molar ratio of M:2L as seen in Figure 2 and as obtained from the previous potentiometric and conductometric studies.
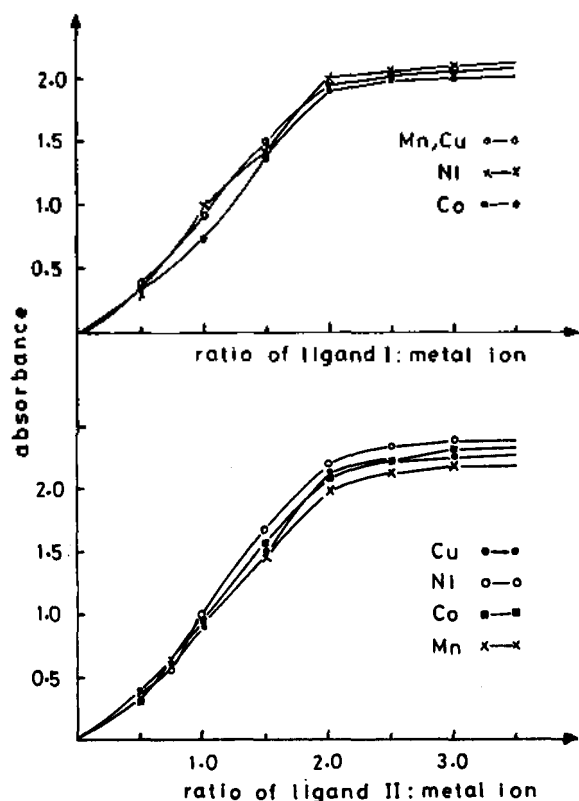

Figure 2. Photometric titration curves of coumarins I and II with transition metal ions.

In order to ascertain the possible bonding sites, the infrared spectra of free coumarins were compared with those of their complexes. Figure 3 shows the spectra of aminocoumarin and its complexes. The spectra of all samples show a broad and strong band at 3250-3100 cm^{-1} which can be attributed to the stretching vibration of OH group of coordinated water molecules. The spectrum of free ligand demonstrates a strong band at 1710 cm^{-1} which is assigned to νC=O band.[20] In complexation, this band is shifted to lower frequency indicating that the coordination of aminocoumarin probably takes place through the carbonyl group. Several weak bands are appeared in the range 1300 to 1000 cm^{-1} owing to the stretching vibrations of C-O.[21] Little change is observed in the spectra of the corresponding complexes suggesting that there is no bonding between the oxygen atom of coumarin ring and the metal atom in each of the complexes. On the other side, the bending vibration band of NH$_2$ group appearing at 1580 cm^{-1} is lowered by 15 cm^{-1} after complexation assuming that the amino group participates in coordination process.[22]

Figure 4 shows the spectra of other coumarins and their copper complexes. The same behaviour was observed for the carbonyl group and the ring oxygen atom of the different derivatives with the metal ion. The absorption bands of OH group (δ OH~1380 cm^{-1}),[22] C$\equiv$N group (ν CN~2350 cm^{-1}),[20] and COOC$_2$H$_5$ group (ν COOC$_2$H$_5$~1780 cm^{-1}),[21] are weakened and shifted to lower frequencies by complexation suggesting the participation of them in formation of the various copper-coumarin complexes.

The d.c. conductivity in the dark is frequently measured property of organic solids. Many organic compounds are semiconductors.[23] Although organic semiconductors are not yet used in electronic devices, they hold great promise for future applications, especially compounds containing conjugated bonds; -C=C-C=C-.[24] A large number of organic

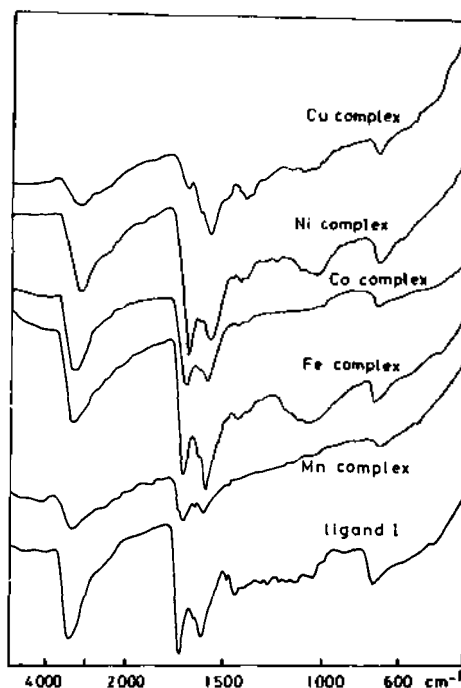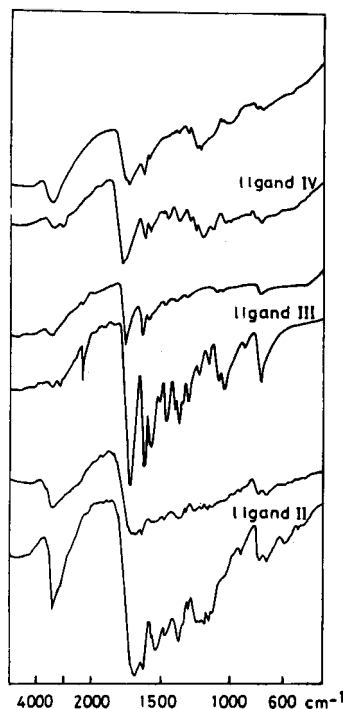**Figure 3.** Infrared spectra of ligand I and its complexes.

Figure 4. Infrared spectra of coumarins and their copper complexes.

Figure 5. Electrical conductivity of coumarins.

compounds are obtained in the form of microcrystalline powder. Consequently, the method of measuring the electrical conductivity of such compounds involves the compacting of the powder.[25]

The conductivity of various coumarins are measured over a relatively moderate temperature range, 298-430 K, to avoid the melting of the samples. The dependance of conductivity, δ, with temperature follows the well known exponential relation: $\delta=\delta^{\circ}$ exp $(-E/kT)$, where E is the activation energy of conduction. The plot of log δ against l/T is shown in Figure 5. The results indicate that the conductivity values of various derivatives, at room temperature, descend as showen:

coumarin IV > coumarin III > coumarin II > coumarin I

This behaviour agrees with the resonance effect (the shift of electrons from one part of a molecule to another) of the substituents, where $COOC_2H_5$ and CN groups have $-M$ and $-I$ effects, *i.e.*, electron acceptor, but OH and NH_2 groups possess $+M$ and $-I$ effects, *i.e.*, electron donor. On other words, the higher resonated coumarins IV and III have higher conductivity values than the lower resonated coumarins II and I, as given in Table 3.

Some irregularities are observed at high temperatures which may be attributed to the change. in structure of coumarins.

The complexation of coumarins with metal ions leads to ascending of the conductivity values. The metal ion in each complex may be act as a bridge facilitating the flow of the electrical charges throughout the coumarin molecule.[26] Room temperature electrical measurements of hydroxy-coumarin complexes are reported: $MnL_2Cl_2 \cdot xH_2O=6.85 \times 10^{-10}$, $FeL_2Cl_2 \cdot xH_2O=6.60 \times 10^{-1}$, $NiL_2Cl_2 \cdot xH_2O=7.29 \times 10^{-10}$ ohm^{-1} cm^{-1}. The small differences in the conductivity values observed indicates that the complexed me-
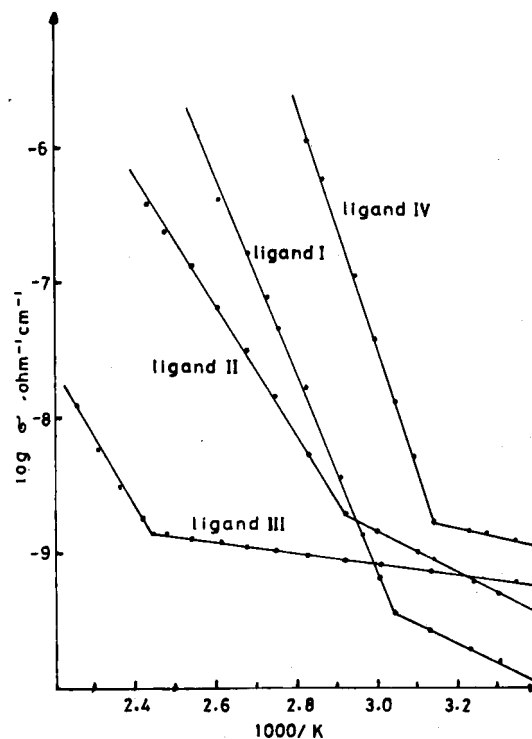
Table 3. Electrical data for coumarins at 298 K

Compounds	δ, ohm^{-1} cm^{-1}	E, eV	W, eV	n, cm^{-3}	μ, cm^2/V.s.
coumarin I	1.26×10^{-10}	0.277	0.304	5.08×10^{20}	1.55×10^{-12}
coumarin II	4.27×10^{-10}	0.307	0.333	1.58×10^{20}	1.69×10^{-11}
coumarin III	5.78×10^{-10}	0.079	0.106	1.14×10^{24}	3.17×10^{-15}
coumarin IV	1.20×10^{-9}	0.119	0.145	2.40×10^{23}	3.13×10^{-14}

tal ions play no part in the conduction process.[27] This suggests that the electrical conduction pathway is predominantly *via* suitable orbitals belonging to coumarin molecules in close proximity to one another.

On the other side, the conductivity values of amino-coumarin complexes are given: $FeL_2Cl_2 \cdot xH_2O=1.12 \times 10^{-9}$, $CoL_2Cl_2 \cdot xH_2O=3.44 \times 10^{-9}$, $CuL_2Cl_2 \cdot xH_2O=7.17 \times 10^{-8}$ ohm^{-1} cm^{-1}. It is clear that the conductivity is higher by 1-2 orders of magnitude than that of uncomplexed aminocoumarin. This behaviour can be attributed to the inclusion of the metal ions into the Π electron delocalization of coumarin I molecules.[28]

Knowledge of the charge carriers concentration, n, and their mobilities, μ, is an essential step towards understanding the mechanism of conduction of coumarins. They were determined using:

$$n = 2 \left(\frac{2\Pi m^+ KT}{h^2} \right)^{3/2} \exp(-E/kT)$$

and $\delta = q\, n\, \mu$

where m^+ is the effective mass of electron and q is its charge. It is obvious that, Table 3, the calculated mobilities are very low. In most organic semiconductors, the carriers

mobility is usually very low.[29] The hopping model is preferable for such compounds, where a carrier can move from one molecule to another by jumping over the barrier *via* an excited state. In this case, the conductivity can be expressed as

$$T = C \exp(-W/kT)$$

C is a constnat and *W* is the activation energy of the hopping process. The difference between the values of energy *W* and *E* gives the activation energy of mobility which is about 0.027 eV for the studied coumarins.

References

1. Sinisterra, J. V.; Marinas, J. M. *Monatsh. Chem.* **1986**, *117*, 111 & **1985**, *116*, 133.
2. Annunziata, R.; Raimondi, L.; Appendino, G.; Gravotto, G.; Palmisano, G. *Gazz. Chim. Italiana* **1995**, *125*, 465.
3. Appendino, G.; Gravotto, G.; Nano, G. M.; Palmisano, G.; Annunziato, R. *Helv. Chim. Acta* **1993**, *76*, 1194.
4. Appendino, G.; Gravotto, G.; Tagliapietra, S.; Ferraro, S.; Nano, G. M.; Palmisano, G. *Helv. Chim. Acta* **1991**, *74*, 1451.
5. Abdalla, M.; El Kady, M.; El Farargy, A. *Egypt. J. Chem.* **1977**, *20*, 245.
6. Kirkiacharian, B.; Serge, D.; Reynaud, P.; Hebed, C. Seanacer, *Acad. Sci., Ser. C* **1979**, *289*, 227.
7. Antonillo, C.; Carlassare, F.; Malier, P.; Siliprandi, P. *Farmaco. Ed. Sci.* **1974**, *29*, 697.
8. Avetisyan, A. A.; Vanyan, E. V.; Cezalyan, D. I.; Galstyan, A. G. *Arm. Khim. Zh.* **1987**, *40*, 239.
9. Irving, H. M.; Rossotti, H. S. *J. Chem. Soc.* **1953**, *3397* & *1954*, 2904.
10. Smith, E. B. *Basic Chemical Thermodynamics*; ELBS & Oxford University Press: Oxford, 1990; p 55.
11. Murakami, S.; Yoshino, T. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2065
12. Willard, H. H.; Merritt Jr., L. L.; Dean, J. A.; Settle Jr., F. A. *Instrumental Methods of Analysis*; D. Van Nostrand, New York, 1981; pp 83, 790.
13. Weller, P. F. *Solid State Chemistry and Physics, An Introduction*; Marcel Dekker, New York, 1973; Ch. 4.
14. Abd El Wahed, M. G.; El Manakhly, K. A.; El. Khososy, N. *Mater. Chem. Phys.* **1995**, *41*, 117.
15. Houghton, R. P. *Metal Complexes in Organic Chemistry*; Cambridge University Press: Cambridge, 1979; pp 49, 50.
16. Lee, J. D. *Concise Inorganic Chemistry*; ELBS & Chapman Hall, London, 1991; p 208.
17. Chiswell, B.; James, D. W. *Fundamental Aspects of Inorganic Chemistry*; John Wiley & Australasia: Sydney, 1969; p 136.
18. Grinberg, A. A. *An Introduction to the Chemistry of Complex Compounds*; Pergamon Press: Oxford, 1962; p 7.
19. Bauer, H. H.; Christian, G. D.; O'reilly, J. E. *Instrumental Analysis*; Allyn and Bacon, Boston, 1978; p 178.
20. Kemp, W. *Organic Spectroscopy*; ELBS & Macmillan, Hong Kong, 1988; p 14.
21. Pavia, D. L.; Lampman, G. M.; Kriz Jr., G. S. *Introduction to Spectroscopy: A Guide for Students of Organic Chemistry*; Saunders Philadelphia, 1979; pp 59, 57.
22. Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*; McGraw Hill: London, 1980; pp 52, 49.
23. Abd El Wahed, M. G. In *Handbook of Advanced Materials Testing*; Edited by Cheremisinoff, N. P.; Cheremisinoff, P. N., Marcel Dekker, New York, 1995; Ch. 16.
24. Yu, P. Y.; Gardona, M. *Fundamentals of Semiconductors, Physics and Materials Properties*; Springer Verlag: Berlin, 1996; p 4.
25. Gutmann, F.; Lyons, L. E. *Organic Semiconductors*; John Wiley: New York, 1967; p 168.
26. El Baradie, K.; Gaber, M.; Abou Sekkina, M. *Thermochim. Acta* **1994**, *246*, 175.
27. Allan, J. R.; Paton, A. D. *Thermochim. Acta* **1993**, *214*, 227.
28. Meier, H. *Organic Semiconductors, Dark and Photoconductivity of Organic Solids*; Verlag Chemie: Weinheim, 1974; p 161.
29. Kao, K. C.; Hwang, W. *Electrical Transport in Solids*; Pergamon Press: Oxford, 1981; Ch. 1.