FINAL REPORT

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MINOR RESEARCH PROJECT IN CHEMISTRY

"DETERMINATION OF STABILITY CONSTANT AND VISCOSITY MEASUREMENT OF LANTHANIDE ION COMPLEXES WITH SUBSTITUTED SCHIFF'S BASES"

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"DETERMINATION OF STABILITY CONSTANT AND VISCOSITY MEASUREMENT OF LANTHANIDE ION COMPLEXES WITH SUBSTITUTED SCHIFF'S BASES"

I. Introduction :

Co-ordination chemistry plays an important role in the chemical industry and life processes. Its importance can be easily realized from the fact that chlorophyll which is vital to photosynthesis in plants is a magnesium complex and hemoglobin which carries oxygen to animal cell, is an iron complex, myoglobin, cytochromes, vitamin B12, etc. are some other examples of bioinorganic origin.

Importance of Co-ordination complexes:

1. Many chelates used s drugs on account of their ital important of their vital important therapeutic role.
2. Coordination compounds are used in analytical chemistry, water softening, food preservation, medicine, ion, exchange resins, antioxidants, electroplating, etc.
3. Citric Acid, Malic Acid, Tartaric Acid etc. which are natural chelating agents help to keep metal ions in body fluids without precipitation.
4. Some of the chelating agents are used for studying functions of metals and enzymes in biological media and also for removal of undesirable and harmful metals from living organisms.

Hankare[1] has studied stability constants and thermodynamic parameters of divalent metal ions with diacetyl monoxide in water-ethanol mixture.

Lingaiah and Anandan[2] have investigated the stability constants of substituted hydroxy phenyl pyrazoles with some divalent transition metal ions.

Sawalakhe and Narwade[3] have studied the metal-ligand stability constants of La(III), Pr(III), Sm(III) metal ions with some substituted pyrazoles.

Jamode et al[4] have investigated –chemical study of substituted pyrazoles pH-metrically.

Agrawal[5] has determined metal-ligand stability constant at 0.1 M ionic strength of transition metal ions with some substituted thiozoles.

Karthikeyan et al[6] have studied a synthesis of some pyrazoles and indazoles and their microwave phenomenon.

However, a detailed study of substituted (Schiff's bases) under identical set of experimental conditions which would ever many fold aspects of complexation is still lacking. The present work is therefore, undertaken to make a systematic study of the ehelates in aqueous solution as well as in different organic solvent-water medium by pH-metry and spectrophotometric technique. In our present investigation following ligands (chelating agents prepared by standard methods[10] are used.

1. 2-hydroxy-3-bromo-5chloro-1- (α – para nito phenyl imino) ethyl benzene-Ligand (L1)
2. 2-hydroxy-3-bromo-5-chloro-1- (α-meta nito phenyl imino) ethyl benzene-Ligand (L2)

Metal ions used in the present work are Tb(III) and Dy(III).

The pH-metric data of pK and log K values of various systems are used.

i. to understand the effect of substituting group on the proton-ligand stability constants (pK) and metal-ligand stability constants (log K) of the complexes.
ii. to test the relation log K = a . pK + b for substituted Schiff's bases.
iii. to check the validity of Hammett's equation for proton-ligand and metal-ligand systems.

Metal-Ligand Complexes in Solution and their Stability Constants:

Rossotti and Rossotti[8] have defined a complex as a species formed by the association of two or more simple species each capable of independent existence; when one of the simpler species is a metal ion, the resulting entity is known as metal complex. The term ligand is sometimes is applied to particular atom is molecule by means of which it is attached to central metal atom or it may be applied to molecule as a whole. Some ligands are attached to metal atom by more than one donor atom in such a manner as to form heterocyclic ring. This is known as Chelation. Because of remarkable properties as high stability,

chelates have been studied in solution as well as in solid state by many workers. The extensive work in coordination complexes has been made possible with the help of various experimental techniques and has led to number of imperial conclusion which have been detailed by Martell and Calvin.[9]

Experimental Procedure for Studying Metal-Ligand stability Constants:

Bjerrum's pH-metric titration process is carried out in the present investigation of project work.

pH-Metric titrations of

i. Perchloric acid (1 x 10^{-2} M)
ii. Perchloric acid (- x 10^{-2} M) and the ligand (20 x 10^{-4} M)
iii. Perchloric acid (1 x 10^{-2} M), the ligand (20 x 10^{-4} M) and the metal salt (4 x 10^{-4} M).

Against standard sodium hydroxide solution (0.195 to 0.202 N) carried out in 10% DMF-water mixture, Ionic strength of solution was maintained constant (μ=0.1 M) by adding an appropriate amount of 1 M $NaClO_4$ solution. Following constants were determined in the present work-

a) pK values of substituted 2-hydroxy ethyl benzene i.e. Ligand (L_1), Ligand (L_2), Liand (L_4) in 70% DMF-water mixture.
b) log K values of rare earth metals La(III), Nd(III), Pr(III), Sm(III) and Tb(III) chelates with ligands mentioned under (a).

The result are discussed accordingly. The pH-metric titration data for same systems are presented in Tables 1, 2 and 3. The graphs are plotted between pH of solution and volumes of NaOHin ml.

The curves are designated as –

i. Acid titration curve (A)
ii. Acid + ligand titration curve (A+L) and
iii. Acid + Ligand + Metal titration curve (A+L+M)

Calculation of Proton-Ligand Stability constants (pK Values):

The proton-ligand stability constants or dissociation constants of substituted Schiff's bases were determined pH-metrically in 70% DMF-water mixture.

Calculation of Metal-Ligand Stability Constants :

The suitable method for the calculations of metal-ligand stability constants for any particular system will be decided by

I. the symmetry of the corresponding formation curve about its mid point.
II. the stability constant values of 1:1 and 1:2 complexes, which can be obtained from the mid point slope of the formation curve (n versus pL)
III. the availability of n values in the low (L) region.

The formation curves differ from each other considerably in symmetry and other characteristics. Therefore, n uniform method of calculations can be employed. Each metal-ligand system is to be treated separately. It is, however, necessary, to know the highest value of N or the formula of the highest complex formed, it is necessary to know the n values at the pH of hydrolysis and precipitation.

The following methods were used for calculation of stability constants –

a) Half Integral Method :-

The values of log K_1 (pL_1) and log K_2 (pL_2) are calculated from the formation curves by known values of pL at which n =0.5 and n = 1.5 respectively.

b) Half Integral Method :-

i) Metal ligand stability constant for 1:1 complex was calculated by using the expression,

$$\log\left[\frac{n}{1-n}\right] = \log k_1 - pL$$

The linear equation as solved for different values of n and pL. The average of the values were taken as correct value of log K_1. The values of n were selected in the range 0.2 to 0.8.

ii) Metal-ligand stability constants for 1:2 complex formation were calculated by above expression; which can be used for obtaining the values of log K_2. As the observed n values will be the sum of first and second complex, the value of n due to second complex will be equal to (n-1) in the region 1<n<2. The above expression can be written as,

$$\log\left[\frac{n-1}{2-n}\right] \log k_2 - pL$$

The n values were selected in the range 1.2 to 1.8. These values are in agreement with the reported values. If the values of a more than 1.00 are not available, log K_2 values are obtained by following expression.

$$2pL_{n=1} = \log K_1 + \log K_2$$

The values of log K_1 and log K_2 for some systems obtained by two methods are found to be in good agreement.

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VISCOSITY MEASUREMENT AT DIFFERENT CONCENTRATION OF LIGAND

Viscosity measurement like other transport properties of electrolyte, provides useful information about solute – solute and solute – solvent interaction. These interactions have been studied in aqueous and non-aqueous solutions by many workers.[1..3] Molecular interactions of electrolyte in binary mixture of two liquids in terms of viscosity B-coefficient have been studied by Kapadi et al[4], Mehrotra et al[5] , Das et al[6] and Nikam et al[7]. Molecular interaction of binary mixtures are also studied by Yadav[8], Kalra et al[9], Pandey at al[10] and Raut et al[11].

The Jones-Dole[12] equation accounts for the observed viscosity concentration dependence of dilute electrolyte solutions, while Nreslau-Miller[13], Vand[14], Moulik[15], Thomson[16] and Einstein[17] equations account for the concentration dependence of viscosity in concentrated electrolyte solutions. Agrawal et al[18] have studied thermodynamic parameters of substituted 2.3-propane dione. Many attempts have been made to study viscosities of binary liquid mixtures. But no satisfactory result seems to have been obtained, especially for ligand systems showing appreciable departure from ideal behaviour[19].

The presents study deals with the viscosity study of Ligand (L_1), Ligand (L_2), in 70% DMF-water mixture at different concentration and at 304 ^{0}k. The data obtained have been used to compute molecular interactions in terms of viscosity B-coefficient of different ligands.

EXPERIMENTAL:

The solvents N-N dimethyl formamide AR grade (purity 99.9%) and doubly distilled water was used. Weighing was made on Mechaniki Zaktady Precyzyjnej Gdansk Balance, made in Poland (±0.001 gm). Densities of solutions were determined by a bicapillary Pyknometer (±0.001 gm) having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1 mm and calibrated with deionised doubly distilled water. The accuracy of density measurement was within ±0. 1 Kgm^{-3}. The viscosities were measured by means of Ostwald's Viscometer thoroughly cleaned and dried. The viscometer was kept in Elite thermostatic water bath and temperature variation was maintained

within ±0.1 ^{0}C. Each measurement, sufficient time was allowed to attain thermal equilibrium between viscometer and water bath. The accuracy of measurement was within 0.11%Kgm^{-1}s^{-1}

RESULTS AND DISCUSSION:

The relative viscosity of each solution in determined by following empirical formula –

$\eta_r = \frac{ds \text{ x } ts}{(dw \text{ x } tw)}$ Where, η_r is relative viscosity of ligand solution

ds is density of ligand solution

dw is density of distilled water

ts is time of flow for solution

tw is time of flow for distilled water

The relative viscosity and density data for different ligands at different concentrations are presented in Tables 1 to 3.

The relative viscosities have been analysed by Jones-Dole equation[12]

$\frac{\eta_r - 1}{\sqrt{c}} = A + B\sqrt{c}$

Where, c is molar concentration of the ligand solution

A is the Falkenhagen coefficient which is the measure of solute – solute interactions and B is the Jones-Dole coefficient which is the measure of solute – solvent interaction.

In the present study, relative viscosity of ligand solutions increases with increase in the concentration of ligand. The increase in viscosity with increase in concentration may be attributed to the increase in solute – solvent interactions. From the graph of (η_r -1/$\sqrt{c}$) versus $\sqrt{c}$, 'A' which is the measure of solute-solute interactions and 'B' which is the measure of solute-solvent interactions has been calculated.

The A and B coefficient values are listed in table 4.

The large and small values of 'A' show the stronger and weaker solute-solute interactions respectively. Solutes with positive viscosity B-coefficient are characterized as "Structure formers" and will impose a new order by reorientation of the adjacent water molecules. The B-coefficient values are +ve for all the systems. This showed stronger interaction between solute and solvent. Such types of results are also shown by Pandey et al[20].

Table – 1

Determination of Relative and Specific Viscosities at different Concentration.

System : Ligand (L_1)

Temp : 31± 0.1^{O}C Medium : 70% DMF-Water

Conc. (C) (m)	$\sqrt{C}$	$\sqrt{C}$ x 10^{-2}	Time Flow Sec	Density d x 10^3 (Kg.m^{-3})	η_r	Specific Viscosity $\eta Sp = \eta_r - 1/\sqrt{c}$ p_a-s
0.010	0.1000	10.00	57.7	0.9652	2.1978	11.9785
0.008	0.0894	8.94	56.2	0.9645	2.1392	12.7423
0.006	0.0774	7.74	55.8	0.9633	2.1213	14.4869
0.004	0.0632	6.32	53.7	0.9622	2.0391	16.4419
0.002	0.0447	4.47	48.5	0.9613	1.8399	18.7897

Table – 2

Determination of Relative and Specific Viscosities at different Concentration.

System : Ligand (L_2)

Temp : 31± 0.1^{O}C Medium : 70% DMF-Water

Conc. (C) (m)	$\sqrt{C}$	$\sqrt{C}$ x 10^{-2}	Time Flow Sec	Density d x 10^3 (Kg.m^{-3})	η_r	Specific Viscosity $\eta Sp = \eta_r - 1/\sqrt{c}$ p_a-s
0.010	0.1000	10.00	57.4	0.9657	2.1875	11.8755
0.008	0.0894	8.94	55.5	0.9648	2.1132	12.4616
0.006	0.0774	7.74	53.1	0.9635	2.0191	13.1662
0.004	0.0632	4.47	48.5	0.9613	1.8399	18.7897
0.0002	0.0447	4.47	44.4	0.9614	1.6846	15.3149

Table –3

A and B Coefficient Values

Systems	A Coefficient	B Coefficient
Ligand (L_1)	18.30	+72.7273
Ligand (L_2)	17.60	+57.6923

VISCOSITY MEASUREMENT AT DIFFERENT TEMPERATURE

The structure of making and breaking properties of liquids, have been considered as a measure of solute-solute and solute-solvent interactions[21,22]. Bary and Irving[23] determined the viscosities of concentrated aqueous electrolyte solution at various concentrations. The relative viscosities of ternary, aqueous, mixed electrolytic solutions for the system KRr-NaBr, KBr-Bu_4NBr, NaCl-NaBr and NaCl- Bu_4NBr at various constant ionic strengths with varying electrolyte mole fractions (at 25 ^{O}C) have been determined by Patil[24]. Pandey Yasmin[25] have measured viscosities and densities of aqueous binary electrolyte solutions of different molalities. Mahajan[26] have studied viscosity B-coefficient of sulphonic acid ligands in different percentages of dioxane-water mixtures. Sondawale[27] have also studied the viscosity at different temperature using 20% dioxane-water and methanol-water mixtures. Recently, Agrawal[28] have determined the viscosity and some thermodynamic parameters in 70% acetone-water mixture.

EXPERIMENTAL:

The solvents N-N dimethyl formamide AR grade (purity 99.9%) and doubly distilled water was used. Weighing was made on Mechaniki Zaktady Precyzyjnej Gdansk Balance, made in Poland (±0.001 gm). Densities of solutions were determined by a bicapillary Pyknometer (±0.001 gm) having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1 mm and calibrated with deionised doubly distilled water. The accuracy of density measurement was within ±0. 1 Kgm^{-3}. The viscosities were measured by means of Ostwald's Viscometer thoroughly cleaned and dried. The viscometer was kept in Elite thermostatic water bath and temperature variation was maintained within ±0.1 ^{0}C. Each measurement, sufficient time was allowed to attain thermal equilibrium between viscometer and water bath. The accuracy of measurement was within 0.11%$Kgm^{-1}s^{-1}$. Different constant temperatures were maintained with the help of elite thermostatic water bath (±0.1^{O}C). For each measurement, sufficient time was allowed to attain thermal equilibrium.

Following ligands are used in the present study.

1. Ligand (L_1) 2. Ligand (L_2)

Table – 4

Determination of Relative Viscosities at different Temperatures

System : Ligand (L_1)

Conc : 0.01 M Medium : 70% DMF-Water

Temp. ^{o}K	$\frac{1}{T}$ x 10^{-3}	Density d x 10^3 ($Kg.m^{-3}$)	$\eta_r = \frac{\eta}{\eta_0}$	log η_r
301.5	3.3167	0.9691	2.4318	0.3859
304.5	3.2841	0.9682	2.2653	0.3551
307.5	3.2520	0.9673	2.0992	0.3221
311.0	3.2154	0.9662	1.9373	0.2872
315.0	3.1746	0.9652	1.7604	0.2456

Table – 5

Determination of Relative Viscosities at different Temperatures

System : Ligand (L_2)

Conc : 0.01 M Medium : 70% DMF-Water

Temp. ^{o}K	$\frac{1}{T}$ x 10^{-3}	Density d x 10^3 ($Kg.m^{-3}$)	$\eta_r = \frac{\eta}{\eta_0}$	log η_r
301.5	3.3167	0.9697	2.4526	0.3896
305.5	3.2733	0.9682	2.2563	0.3534
309.5	3.2310	0.9670	2.1165	0.3256
313.5	3.1898	0.9654	1.9339	0.2864
317.5	3.1496	0.9638	1.8053	0.2566

Table –6

Values of Thermodynamic Parameters

Medium – 70% DMF - Water

Systems	Δ G (J $mole^{-3}$ k^{-1})	Δ H (J $mole^{-3}$ k^{-1})	Δ S (J $mole^{-3}$ k^{-1})
Ligand (L_1)	-19147.142	18806.25702	123.2201
Ligand (L_2)	-14770.6798	15082.1551	96.5469

RESULTS AND DISCUSSTION:

The viscosity of a liquid generally decreases with rise in temperature. The decrease is appreciable being about two% per degree rise of temperature in many cases. This has been explained in terms of 'hole theory' of liquids. According to this theory, there are vacancies or holes in a liquid. The liquid molecules keep on moving continuously into these vacancies also keep on moving around as otherwise the liquid will not be able to flow. This process however, requires energy. A liquid molecule, therefore, needs some energy to move into hole. As the energy becomes increasingly available at increasing temperature, a liquid can flow more easily at higher temperature. The coefficient of viscosity, thus, falls appreciably with rise in temperature as presented in table 4 & 5.

The relationship between coefficient of viscosity of a liquid and temperature is expressed mathematically as –

$\eta_r = A.\, e^{-\Delta G/RT}$

The graphs are plotted between log η and 1/T.

The thermodynamic parameters were calculated by using following expressions –

$\Delta G = -2.303\ R \times slope$

$\log \eta_{r\,1} - \log \eta_{r\,2} = [\Delta H/2.303]\ [1/T_1 - 1/T_2]$

and $\Delta S = (\Delta G - \Delta H) / T$

These thermodynamic parameters for different systems are listed in Table 4

The positive and negative values of entropy indicate that reaction may be exothermic and endothermic respectively. Burghate et al[29] have also done thermodynamic studies in 70% dioxane-water. Arbad et al[30] and many workers[31-35] have also studied viscosity at different temperature.

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