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Conductometric Studies on Temperature Dependence and Thermodynamics of Ion-Association of Leucinato*bis*(biguanide) Cobalt(III) Complexes

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The conductivity measurements over a wide range of temperatures between 5 to 50 ºC were made in dilute aqueous solutions of the chloride and bromide of leucinato*bis*(biguanide) cobalt(III) complexes. The ion-association constants (K_A) obtained by using the method of Jenkins and Monk had minimum values at temperatures (t_{min}), characteristics of the anions. The remarkable increases of the K_A values with decreasing temperatures below (t_{min}), were ascribed due to specific short range interactions between the amino-acid ligands of the complexes and halide atoms of the anions in the contact ion pairs. The thermodynamics properties *viz.* changes in entropy, enthalpy and free energy which enable to study the nature of the ion-association had also been calculated using the values of K_A. Using Stoke's law and Bjerrum relationship, the sizes of the ion-pairs had also been calculated.

Key Words: Ion association constants, Thermodynamic parameters, Stoke's law, Bjerrum equation, Leucinato*bis*(biguanide) cobalt(III) chloride and bromide, Conductivities.

INTRODUCTION

Measurements of conductivities over a wide range of temperatures for electrolyte solutions can give detail information on ion-ion and ion-solvent interactions[1-3]. From the conductivity measurements, the values of K_A obtained by using Jenkins and Monk[4] had, minimum values at characteristic temperatures (t_{min}). These were interpreted by assuming at specific short range interactions between the ions due to their weak hydration complex ions with various anions have been investigated conductometrically[5-7] but not including their temperature dependence.

Yokoyama and co-workers[8-11] had studied conductometrically the ion-pair formation of some cobalt(III) complex ions with various anions between the temperature range 0-50 ºC. So far no studies have been made on temperature dependence of the ion-association of cobalt(III) complexes containing biguanide as primary ligand and amino acid as secondary ligand is concerned. In the present study, conductivity of aqueous solutions of chloride and bromide of leucinato*bis*(biguanide) cobalt(III)

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complexes have been measured in temperature range of 5 to 50 ºC. From such data, entropy, enthalpy and free energy changes can be estimated which enable the nature of the ions to be probed. Using stoke's law and Bjerrum equation[11,12], the sizes of ion pairs have been calculated.

EXPERIMENTAL

Leucinato*bis*(biguanide) cobalt(III) chloride and bromide were prepared following the procedures described in literature. The complexes were recrystallized twice from hot water (conductivity water) and their purity was examined by conventional chemical analysis and spectral measurements. The values were in good agreement with literature values[13].

Conductivity measurements: Conductivity measurements of the complexes at different low concentrations on conductivity water of low specific conductance ($< 4 \times 10^{-6}$ Ω), were made at IKH_Z with D.D.R. Conductivity Meter Type 304 (Systronics) with thermostatic bath (Mode D 8-G of Hakke Mess-technic), between 5 to 50 ºC and accomplishes within 5 h after the preparation of the solutions. The precision of the temperature measurement was ± 0.003 ºC and the accuracy of temperature was ± 0.01 ºC and governed by the thermostat.

RESULTS AND DISCUSSION

Evaluation of association constants: The conductivity data was analyses in the same manner as described previously[13-15] assuming the following ion-pair formation.

$$[Co(leu)(BigH)_2]^{2+} + X^- \rightleftharpoons \{[Co(leu)(BigH)_2]^{2+}x\}^+$$

(x = Cl^- or Br^-) where triple ion formation was regarded as being negligible in the dilute solutions investigated[10-16]. The calculated ion-association constants for the complexes are given in Table-1. The K_A values at any temperature are given in Table-1. The K_A values of Br^- complex greater than Cl^- complex at any temperature.

TABLE-1
ASSOCIATION CONSTANT (log K_A) FOR $[Co(leu)(BigH)_2]X_2$ (X = Cl or Br)
AT DIFFERENT TEMPERATURES

Compd.	Temperature (ºC)									
	5	10	15	20	25	30	35	40	45	50
Chloride	2.66	2.63	2.59	2.55	2.51	2.48	2.47	2.49	2.53	2.58
Bromide	2.61	2.57	2.54	2.51	2.47	2.45	2.46	2.48	2.51	2.54

Ion-association and their temperature dependence: The plots of log K_A *vs.* temperature (t ºC) are showing in Fig. 1. The association constants, K_A has minimum values at (t_{min}) characteristic of the anions. The t_{min} increased in the order $Cl^- > Br^-$.

The log K_A temperature dependence can be reproduced by a quadratic equation in t as eqn. 1:

$$\log K_A = p(t-t_{min})^2 + \log K_{A(min)} \qquad (1)$$

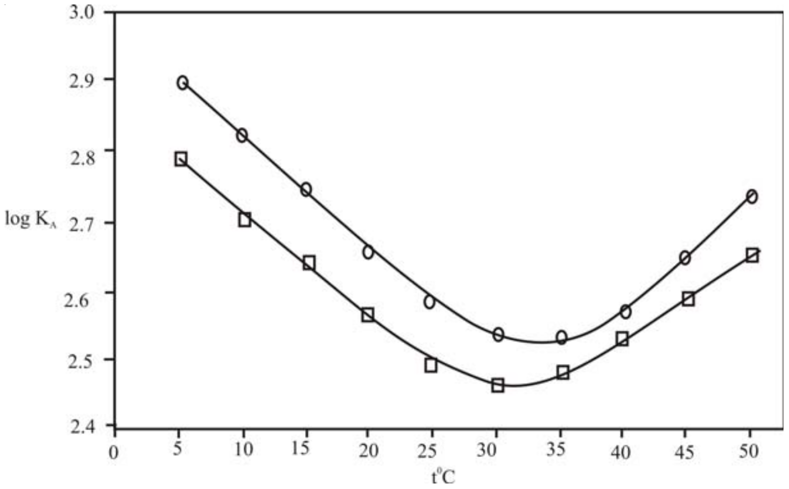

Fig. 1. Temperature dependence of the ion-association constants log K_A, between $[Co(leu)(BigH)_2]^{2+}$ and the monovalent anions, chloride (□) and bromide (○)

where log $K_{A(min)}$ are the minimum values of log K_A, t_{min} are the temperatures giving log $K_{A(min)}$ and P corresponds to the curvature of a parabola.

The expression for the standard entropies and enthalpies are expressed as:

$$\Delta S^o_{ass(aq)} = 2.303R\{\log K_{A(min)} + p(3t-t_{min} + 546.3)\ (t-t_{min})\} \quad (2)$$

$$\Delta H^o_{ass(aq)} = 4.605\ Rp\ (t + 273.15)2\ (t-t_{min})\} \quad (3)$$

Knowing the values of $\Delta S^o_{ass(aq)}$, $\Delta H^o_{ass(aq)}$ and the standard free energy change, $\Delta G^o_{ass(aq)}$ can be calculated from.

$$\Delta G^o_{ass(aq)} = \Delta H^o_{ass(aq)} - T\Delta S^o_{ass(aq)} \quad (4)$$

The calculated values of $\Delta S^o_{ass(aq)}$, $\Delta H^o_{ass(aq)}$ and $\Delta G^o_{ass(aq)}$ at several temperatures are given in Table-2. The values of $\Delta S^o_{ass(aq)}$ and $\Delta H^o_{ass(aq)}$ are in the order $Cl^- > Br^-$ as expected trend[14].

TABLE-2
THERMODYNAMIC PARAMETERS OF (log K_A) FOR $[Co(leu)(BigH)_2]X_2$, (X = Cl or Br) AT DIFFERENT TEMPERATURES

Compound	Temperature (°C)									
	5	10	15	20	25	30	35	40	45	50
$[Co(leu)(BigH)_2]Cl_2$										
ΔS^o_{ass} (J d^{-1} mol^{-1})	-12.96	-1.79	-0.99	-1.613	-0.117	2.90	–	11.50	17.59	16.65
ΔH^o_{ass} (kJ mol^{-1})	-17.77	-18.41	-19.07	-18.75	-14.63	7.03	–	5.01	31.00	28.78
ΔG^o_{ass} (kJ mol^{-1})	-14.16	-17.91	-18.49	-18.28	-14.59	6.15	–	11.42	25.40	23.41
$[Co(leu)(BigH)_2]Br_2$										
ΔS^o_{ass} (J d^{-1} mol^{-1})	-3.74	-1.07	-2.48	-1.65	-0.19	–	6.50	8.75	17.94	11.70
ΔH^o_{ass} (kJ mol^{-1})	-22.76	-18.41	-20.50	-18.09	-13.61	–	-2.18	7.50	16.27	18.39
ΔG^o_{ass} (kJ mol^{-1})	-21.72	-18.11	-19.78	-17.61	-13.55	–	0.18	4.82	12.47	14.28

The presence of t_{min}, was explained due to the weak hydration of the anions related to their structure breaking properties[14]. The increases in the values of association constants beyond t_{min} is supported by increase of entropy changes. A positive entropy change has been explained on the assumption that the 'ice-berg' structure around the cation is broken when the association takes place leading to the increase in the degree of disorderness[7-10]. The remarkable increase of the K_A values before reaching t_{min}, with decreasing temperatures may be ascribed to specific short-range interactions[14]. Between the amino hydrogen atoms of the leucinato and biguanide ligands and amino hydrogen atoms of the complexes and the halide atoms of the anions in the contact ion-pairs.

Further, Mishra and Singh[18] found that in the case of (2-guanidinium benzimidazole) chromium salts, the value of K_A decreases with rise in temperature. They suggested that the value of K_A decreases with rise in temperature and the breaking of the solvent structure around the complex cation is not the predominant phenomenon of their system and treated them to have obeyed the simple law of increasing dissociation at higher temperature. Similar phenomenon was observed in previously[9].

Evaluation of sizes of ion-pairs: The sizes of ion-pairs have been calculated from Bjerrum equation[13]:

$$K_A = \frac{4\pi N}{1000}\left[\frac{|Z_1Z_2|e^2}{DKT}\right]^3 Q(b) \qquad (4)$$

$$Q(b) = f_2^b y^{-4} e^y dy$$

$$y = \left[\frac{|Z_1Z_2|e^2}{DrKT}\right]; b = \left[\frac{|Z_1Z_2|e^2}{DaKT}\right]$$

where 'a' the distance of closed approach to ions forming the ion-pairs. The value of Q(b) were calculated from the values of K_A (experimental). From the Q(b) values, the values of b was obtained from the standard table[11] and hence 'a' can be calculated as Table-3.

The ionic radii 'a' have also been calculated using Stoke's law[11] as in Table-3.

$$a = \frac{9.1\times10^{-7} Z_i}{\Lambda_i}$$

where, a = radius of ion. Z_i = valency of the ith ion, Λ_i = limiting conductivity of the ith ion.

The approximate radii of $\{[Co(leu)(BigH)_2]^{2+}$ and ion pair $\{[Co(leu)(BigH)_2]x\}^{+}$, where obtained from Stoke's law and Bjerrum equation, have been compared in[3].

The sizes of the ion pairs for Cl^- and Br^- complexes are comparable if we assume their stokes sizes. Sizes of the ion-pairs calculated from Bjerrum equation and stoke's law do not agree well. However such discrepancies have also been reported by the earlier workers[5,7,9,12], with no proper explanation and yet to be studied.

TABLE-3
APPROXIMATE RADII OF $[Co(leu)(BigH)_2]^{2+}$, $\{[Co(leu)(BigH)_2]Cl\}^{+}$ AND $\{[Co(leu)(BigH)_2]Br\}^{+}$ AT DIFFERENT TEMPERATURES

	Stoke's law – Bjerrum equation (Å)				
	Temperature (ºC)				
	5	10	15	20	25
$[Co(leu)(BigH)_2]^{2+}$	3.915-0.00	3.70-0.00	3.52-0.00	3.30-0.00	3.12-0.00
Cl^-	1.930-0.00	1.68-0.00	1.49-0.00	1.33-0.00	1.17-0.00
Br^-	1.890-0.00	1.66-0.00	1.47-0.00	1.29-0.00	1.197-0.0
$\{[Co(leu)(BigH)_2]Cl\}^{+}$	6.570-1.83	5.95-1.86	5.59-1.91	5.23-1.97	5.00-2.02
$\{[Co(leu)(BigH)_2]Br\}^{+}$	5.130-1.81	4.79-1.86	4.41-1.93	4.16-2.07	3.95-2.27
	Temperature (ºC)				
	30	35	40	45	50
$[Co(leu)(BigH)_2]^{2+}$	2.95-0.00	2.780-0.00	2.78-0.00	2.59-0.00	2.39-0.00
Cl^-	1.08-0.00	0.991-0.00	0.91-0.00	0.84-0.00	0.78-0.00
Br^-	1.60-0.00	0.992-0.00	0.91-0.00	0.84-0.00	0.78-0.00
$\{[Co(leu)(BigH)_2]Cl\}^{+}$	4.64-2.06	4.360-2.16	4.57-2.15	3.78-1.62	3.44-2.05
$\{[Co(leu)(BigH)_2]Br\}^{+}$	3.76-2.12	3.480-2.22	3.27-2.17	3.10-2.30	2.91-2.30

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