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Studies on ion-pairing effects of the kinetics of aquation of bromopentaammine cobalt(III) complex in malonate media

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ARTICLE INFORMATION

ABSTRACT

The aquation of bromopentaamminecobalt(III) ion in the presence of ion-pairing malonate anion in mixed solvent media of water with tert-butanol (10%:50%, v:v) have been investigated spectrophotometrically at different temperatures (30-60 °C). Nonlinear plots of Log (k_{ip}) ion-pair rate constants against the reciprocal of the dielectric constant D, Log of water concentration and Grunwald-Winstein Y values were found. The thermodynamic and extrathermodynamic analyses of the kinetic data have been discussed in terms of solvent effect on the ion-pair aquation reactions. The obtained isokinetic temperatures of these systems indicate the existence of compensation effect arising from solute-solvent interaction. The extrema found in the change of ΔH_{ip}^* and ΔS_{ip}^* with the mole fraction of the co-solvent can be attributed to the change of the physical properties of the solvent-water mixture with the solvent structure. Application of a free energy cycle is performed to compare between the stability of the initial and the transition state of the complex. However, small changes in ΔG_{ip}^* with the mole fraction of the co-solvent was found, indicating a compensating effects between ΔH_{ip}^* and ΔS_{ip}^*.

1. Introduction

Transition metal complexes play a variety of important roles in biological systems. The biological activities of cobalt complexes have been the subject of studies on the inhibition of rabbit brain and the inhibition of soybean lipoxygenase enzyme [1-2]. Also cobalt(III) is beneficial for human since it is a part of vitamin B_{12} [3].

Different studies had described the kinetics of aquation of halogenopentaamminecobalt(III) in different media [4-8]. Such investigations include numerous factors, describing preferential, selective and specific solute-solvent interactions and are useful in accounting for the equilibrium behavior of electrolytes in solution. It was shown [9] that the ion-pairs formed between some bivalent anions and halopentaammine cobalt(III) and chromium(III) cations undergo aquation at a faster rate compared to the free cations. It was found that [10] the ion-pairing effects on the rate of aquation of bromopentaammine cobalt(III) perchlorate in 20% (v/v) ethylene glycol solutions of some dicarboxylates must follow Waytt and Davies [11] treatment for calculating the ion-pair rate coefficients. It is fairly established that halopentaammine cobalt(III) complexes aquated by an essentially dissociative process [12].

The aim of the present work is to study of the aquation of bromopentaamminecobalt(III) perchlorate in malonate buffer solutions [0.008-0.040 mol/L malonic acid neutralized by 80% Na_2CO_3 containing tert-butanol (10%:50%, v:v)] in an attempt to determine the solvent effects on thermodynamic and extrathermodynamic parameters of activation where the data

can be linked to obtain information about the solute-solvent interaction.

2. Experimental

2.1. Reagents

Cobalt(II) carbonate, hydrobromic acid 48%, ammonia, malonic acid, sodium carbonate and tert-butanol were purchased from Fluka Chemika. Hydrogen peroxide, were purchased from Riedel-de Haën. Hydrochloric acid was purchased from Chemical Management Consulting. Perchloric acid 60% was purchased from Merck. The bromopentaammine cobalt(III) perchlorate complex was prepared by using the method of Hynes [13].

2.2. Procedure

The rate of aquation of $[Co(NH_3)_5Br](ClO_4)_2$ complex in 10%:50% (v:v) of tert-butanol with malonate buffer solution at 30-60 °C was followed spectrophotometrically using Unicam Helios Alpha and Beta spectrophotometer at λ = 250 nm. The spectrophotometer was fitted with thermostated cell holders, heated by water circulating from a Heto HMT 200 thermostat. The inflow and the outflow temperatures were measured and the mean temperature was taken as that of the cell.

Table 1. Values of rate constants (k_ox10^6) in sec^{-1} for the aquation of [Co(NH$_3$)$_5$Br]$^{2+}$ in *tert*-butanol (10-50%) at different temperatures.

T, ºC	10% *tert*-butanol	20% *tert*-butanol	30% *tert*-butanol	40% *tert*-butanol	50% *tert*-butanol
30	2.96	2.68	0.11	0.61	4.45
35	3.32	7.12	0.72	1.09	4.61
40	12.10	17.00	4.83	18.30	9.60
50	92.30	93.90	95.70	44.80	94.20
60	364.00	224.00	227.00	208.00	180.00

Table 2. Values of rate constants (k_{obs}x10^6) for the aquation of [Co(NH$_3$)$_5$Br]$^{2+}$ in malonate media (m$_1$) containing *tert*-butanol (10-50%) at different temperatures.

m$_1$, mol/L	Temperature, ºC				
	30	35	40	50	60
(k_{obs}x10^6) in 10%					
0.008	4.71	14.64	29.17	58.77	473.1
0.016	5.08	11.95	34.06	141.2	394.1
0.024	5.71	17.28	47.44	163.95	469.4
0.032	2.07	26.53	38.78	164.81	546.1
0.04	3.99	20.1	47.34	187.23	546.1
(k_{obs}x10^6) in 20%					
0.008	7.07	10.92	26.31	136.56	439.7
0.016	6.74	11.49	16.17	156.53	416.2
0.024	10.36	15.35	26.67	152.21	391.3
0.032	6.62	14.23	27.28	167.6	530.1
0.04	6.15	12.69	34.400	174.7	437.7
(k_{obs}x10^6) in 30%					
0.008	4.18	7.35	16.75	140.29	422.4
0.016	5.66	8.14	21.39	177.67	382.7
0.024	9.52	5.56	16.66	169.60	522.2
0.032	3.12	19.96	29.11	147.88	420.9
0.04	4.50	26.87	32.01	146.66	471.2
(k_{obs}x10^6) in 40%					
0.008	4.94	15.32	77.16	167.18	617.96
0.016	6.98	10.41	28.44	166.91	506.12
0.024	7.08	24.91	85.99	175.47	548.32
0.032	5.63	23.39	45.65	158.45	450.8
0.04	4.71	13.39	40.42	162.24	436.1
(k_{obs}x10^6) in 50%					
0.008	5.66	11.69	33.095	149.09	414.9
0.016	9.13	18.18	34.61	152.11	383.1
0.024	9.21	19.16	43.76	167.38	405.1
0.032	5.58	24.35	45.77	194.56	442.4
0.04	14.19	24.11	46.3	222.22	428.0

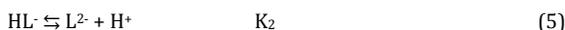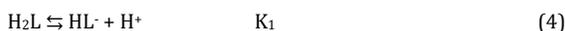## 3. Results and discussion

Plots of log (A$_t$-A$_\infty$) versus time were found to be linear for the aquation of [Co(NH$_3$)$_5$Br](ClO$_4$)$_2$ complex. The observed rate constants are collected in Table 1 and 2.

The ion-pair rate coefficient (k_{ip}) was calculated according to the following Wyatt and Davis equation [11].

$$k_{obs}.m_3 = k_0 [CpX^{2+}] + k_{ip} [CpXL] \qquad (1)$$

where, k_0 - the observed rate constant in the absence of dicarboxylate ion, k_{obs} - the observed rate constant in the presence of dicarboxylate ion, m_3 - the stoichiometric concentration of the complex salt, [CpX^{2+}] - the free complex ion concentration and [CpXL] - the ion-pair concentration. [CpXL] was calculated with the aid of the following equations:

$$CpXL \leftrightarrows CpX^{2+} + L^{2-} \qquad K_D \qquad (2)$$

$$NaL^- \leftrightarrows Na^+ + L^{2-} \qquad K_{NaL^-} \qquad (3)$$

$$H_2L \leftrightarrows HL^- + H^+ \qquad K_1 \qquad (4)$$

$$HL^- \leftrightarrows L^{2-} + H^+ \qquad K_2 \qquad (5)$$

where;

$$K_D = [CpX^{2+}][L^{2-}] \gamma_2^2 / [CpXL] \qquad (6)$$
(L^{2-} represents the dicarboxylate anion)

$$K_1 = [H^+][HL^-] \gamma_1^2 /[H_2L] \qquad (7)$$

$$K_2 = [H^+] [L^{2-}] \gamma_2/ [HL^-] \qquad (8)$$

$$K_{NaL^-} = [Na^+] [L^{2-}] \gamma_2/ [NaL^-] \qquad (9)$$

$$Log \gamma_i = -A (I^{1/2}/ (1+1.3 I^{1/2})-0.3I) \text{ (Debye-Huckle equation)} \qquad (10)$$

(Log γ_2 =4.Log γ_1), (I is the ionic strength γ_1 and γ_2 are the activity coefficients of the univalent and divalent ions, respectively).

$$I = 0.5 ([H^+] + [HL^-] +4[L^{2-}] +4[CpX^{2+}] +2m_3 + [Na^+] + [NaL^{1-}]) \qquad (11)$$

$$m_1= [H_2L] + [HL^-] + [CpXL] + [NaL^-] \qquad (12)$$

$$m_3= [CpX^{2+}] + [CpXL] \qquad (13)$$

The principle of calculations performed by computer programs can be summarized as:

For the first cycle [H$^+$] = 0, [CpXL] = 0, [NaL$^-$] = 0, (14)

$$[CpX^{2+}] = m_3 – [CpXL], [HL^-] =0.5 m_2, [H_2L] = 0.3m_1, \qquad (15)$$

$$[L^{2-}] = m_1 – [HL^-] – [CpXL] – [NaL^-] – [H_2L], \qquad (16)$$

$$[Na^+] = 2m_2 – [NaL^-]. \qquad (17)$$

where, m_2 is the concentration of sodium carbonate.

Afterwards, the ionic strength takes its first approximated value and then γ_1 and γ_2 after which the following terms take their new value;

$$[H^+] = K_2 [HL^-] / [L^{2-}] \gamma_2 \qquad (18)$$

$$[H_2L] = [HL^-][H^+] \gamma_1^2 / K_1 \qquad (19)$$

$$[HL^-] = 2m_1 - 2m_2 - 2[H_2L] - [H^+] \qquad (20)$$

$$[L^{2-}] = m_1 - [HL^-] - [H_2L] - [CpXL] - [NaL^-] \qquad (21)$$

$$[NaL^-] = [Na^+] [L^{2-}] \gamma_2 / K_{NaL^-} \qquad (22)$$

$$[CpXL] = m_3 / [(K_D/\gamma_2^2[L^{2-}]) + 1] \qquad (23)$$

$$[CpX^{2+}] = m_3 - [CpXL] \qquad (24)$$

Then I, γ_1 and γ_2 were recalculated again. These steps of calculations were repeated many times until the difference between two successive values of [CpXL] becomes equal to or less than 10^{-7}. The obtained average values of k_{ip} in malonate media with different percentage of *tert*-butanol are collected in Table 3.

Table 3. Calculated values of rate constants (k_{ip}x10^5) in sec^{-1} for the aquation of $[Co(NH_3)_5Br]^{2+}$ in malonate buffer containing *tert*-butanol (10-50%) at different temperatures.

Temp., ^oC	k_{ip} x10^5 in Malonate buffer at different % of *tert*-butanol				
	10	20	30	40	50
25	9.43	0.39	2.39	0.39	0.71
30	16.46	1.04	4.16	0.86	1.36
35	28.22	2.59	7.10	1.83	2.56
40	47.54	6.32	11.92	3.79	4.73
50	128.60	34.56	32.00	15.26	15.19
60	327.60	170.60	80.98	56.42	45.54

3.1. Variation of Ion-pair coefficients (k_{ip}) with solvent parameters

The effect of water concentration in aqueous organic solvent mixture was investigated by the plot of the Log k_{ip} versus Log [H_2O] at 30 °C. This plot was found to be nonlinear as shown in Figure 1. This nonlinearity confirms that the internal structure of the media studied suffered from serious changes on addition of *tert*-butanol in the presence of malonate buffer, indicating that the hydrogen bond between the organic solvent and the buffer added to water is stronger than between two water molecules. Thus, hydrogen bonding between neighboring water molecules will be replaced gradually by hydrogen bonding with solvent and buffer molecules where the tetrahedral structure of water is largely broken [14].
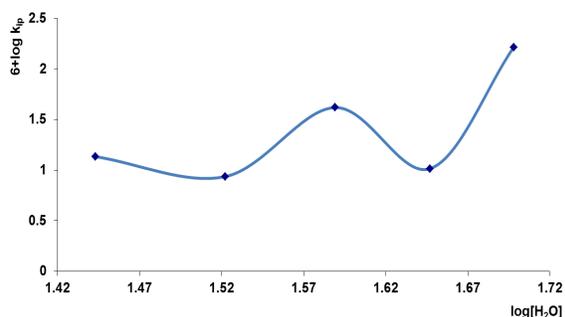

Figure 1. Log k_{ip} versus log [H_2O] at 30 °C at different concentrations of Malanote buffer.

The plot of Log k_{ip} against the Grunwald-Winstein Y-values was found to be nonlinear as shown in Figure 2. This confirms the differential effect of solvent structures between the initial and the transition states.
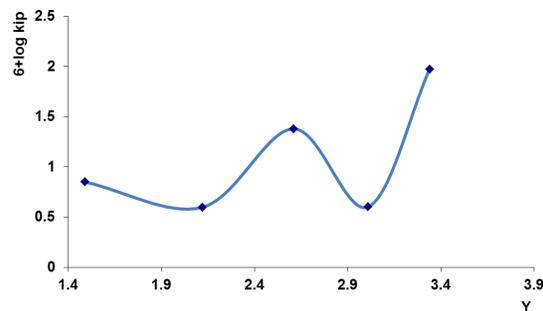

Figure 2. Log k_{ip} versus Y at 25 °C at different concentrations of Malonate buffer.

Tert-butanol has special effect on the formation of ion-pair. This fact was also proven in previous studies [15-16], where it was found that *tert*-butanol has a greater effect on the water structure than the other solvents used earlier due to its branched chain. This may be attributed to the variation of important properties of the medium, such as the structure of the solvent, ionizing power, basicity and dielectric constant, which greatly influence the rate of the reaction. In addition, *tert*-butanol is a dipolar protic solvent [17], since the oxygen atom of an alcohol molecule carries one proton and two lone pairs of electrons, it might the expected to form three hydrogen bonds with its neighbors, but all the evidences show that no more than two bonds are formed, each oxygen acting once as proton donor and once as proton acceptors due to steric effects of the alkyl groups. Also Log k_{ip} was plotted against reciprocal of the dielectric constant D at 25 °C, where the dielectric constant values of different compositions are obtained from Akerlof data [18]. As shown in Figure(3), the plot was found to be non linear in accordance with the general observations found in the aquation of a large number of other cobalt(III) complexes [19-20] in water-cosolvent mixtures, which led to a conclusion, that the contribution of the non electrostatic part of solvent effect, overcomes the electrostatic component part. Also, these parameter measures macroscopic properties, while specific solute-solvent interactions occur on a microscopic scale are completely neglected. In such cases, the differential solvation of the initial and transition states is the controlling factor for the changes in the rate constant [21].
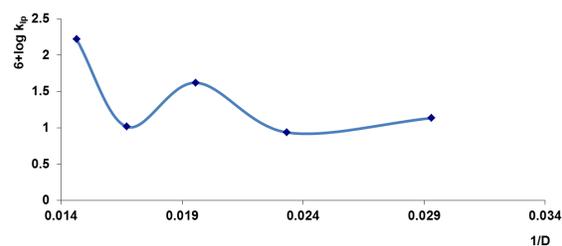

Figure 3. Log k_{ip} versus 1/D at 30 °C at different percentages of *tert*-butanol in Malonate buffer media.

However, Elsemongy and Amira [22] proposed a general equation for the variation of specific rate constant (k) with the dielectric constant (D) for any reaction, in which the transition state may or may not polarized. This equation was proved to be applicable to usual reactions, as well as those exhibiting minima or maxima with solvent composition variation. Their equation takes the following for

$$Log A/K = E.b/2.302.R.Log C/D \qquad (25)$$

$$Log C = Log A + 293.15b \qquad (26)$$

where A is the frequency factor, a and b are Akerlof's empirical constants [17]. The plot Log A/K versus E.b/Log C/D as shown in Figure 4, gives a good straight line with a slope approximately equals to 0.052, which is equal to 1/2.302.R = 0.052. This result adds a further support of the validity of the above equation in the case of aquation of bromo-pentaamminecobalt(III) complex ion in water-*tert*-butanol medium.
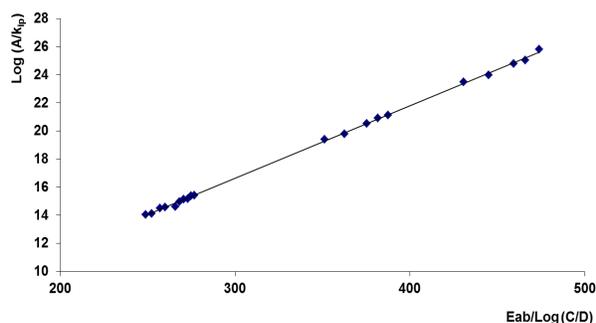

Figure 4. Correlation between the rate constant and the dielectric constant for Malonate buffer.

3.2. Thermodynamic parameters of the ion-pair aquation reactions

The thermodynamic parameters of the activated complex at 40 °C were collected in Table 4.

Table 4. Values of the thermodynamic parameters of the ion-pairing aquation of $[Co(NH_3)_5Br]^{2+}$ in malonate buffer at different mole fraction *tert*-butanol at 40 °C.

Temp., °C	x_2 (Mole fraction)	ΔH_{ip}^* (kJ/mole)	ΔS_{ip}^* (J/K.mole)	ΔG_{ip}^* (kJ/mole)
	0.02	81.11	-49.81	96.69
	0.045	140.23	122.51	101.94
40	0.075	80.50	-63.23	100.29
	0.112	114.42	35.62	103.27
	0.116	95.66	-22.49	102.42

A linear plot of ΔG_{ip}^* against ΔG_{ass}^* (free energy of ion-pair formed) is obtained as shown in Figure 5, which takes the form,

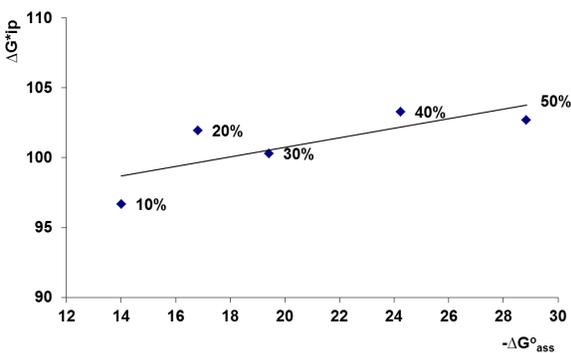$$\Delta G_{ip}^* = a'\Delta G_{ass}^0 + b' \qquad (27)$$

Figure 5. ΔG_{ip}^* versus ΔG_{ass}^* for Malonate buffer at different solvent compositions at 40 °C.

The relationship between the enthalpy of activation ΔH_{ip}^* and the enthalpy of association (ion-pair formation) ΔH_{ass}^0 at different solvent compositions is shown in Figure 6. The plot shows a linear correlation which takes the form of Equation (28):

$$\Delta H_{ip}^* = c\Delta H_{ass}^* + d' \qquad (28)$$

This behavior is due to the interaction between the mixed solvent medium containing the dicarboxylate anions and water. These interactions are attributed to the essentially co-operative nature of hydrogen bonding; together with the unfavorable steric effected of the organic group for both the *tert*-butanol and the malonate buffer. Thus, it restricts the degree of order, which can be established in the liquid state, and precludes the kind of three dimensional associations which is dominant in water.
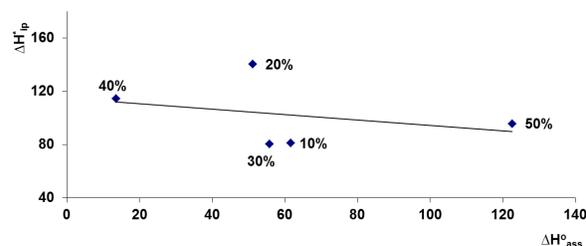

Figure 6. ΔH_{ip}^* versus ΔH_{ass}^0 for Malonate buffer at different solvent compositions at 40 °C.

Finally, the plots of ΔS_{ip}^* versus ΔS_{ass}^0 for different solvent compositions are also found to be linear as represented in Figure 7 according to Equation (29):

$$\Delta S_{ip}^* = e\,\Delta S_{ass}^0 + f \qquad (29)$$

The obtained correspondence suggests that both entropies of activation ΔS_{ip}^* and association ΔS_{ass}^0 are largely charge-controlled.
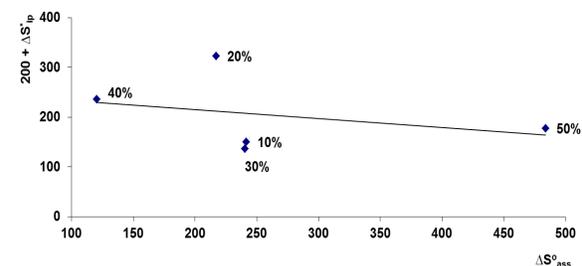

Figure 7. ΔS_{ip}^* versus ΔS_{ass}^0 for Malonate buffer at different solvent compositions at 40 °C.

3.3. Variation of activation parameters with solvent composition

The variation of the thermodynamic parameters of activation ΔG_{ip}^*, ΔH_{ip}^* and ΔS_{ip}^* with the mole fraction of the *tert*-butanol x_2 is introduced in Figure 8 at different composition of *tert*-butanol. ΔH_{ip}^* and ΔS_{ip}^* plots versus mole fraction of the co-solvent x_2 displayed extrema at different values of x_2, indicating that the addition of *tert*-butanol in small amounts plays an important role. This was also observed for trans-$[Copy_4Cl_2]^{1+}$ [23] and $[Co(NH_3)_5Br]^{2+}$ [24] where the structure formation becomes greater at lower values of x_2. At the lower x_2 (between 20% to 30%; v:v of *tert*-butanol), the water is rich in the media where the *tert*-butanol molecules progressively occupy the cavities in the water network without enhancing the water structure. However, with an increase in the *tert*-butanol concentration, the water structure undergoes a gradual disruption and clusters are formed through the formation of hydrogen bonding. By adding more and more *tert*-butanol, it

has characteristics that the alkyl groups cooperative ordering of water molecules by a hydrophobic hydration effect.

The changing of solvent composition has little effect on ΔG_{ip}^* as shown in Table 4 by which linear plots are observed between ΔG_{ip}^* against x_2, indicating the presence of compensation effect between ΔH_{ip}^* and ΔS_{ip}^*.
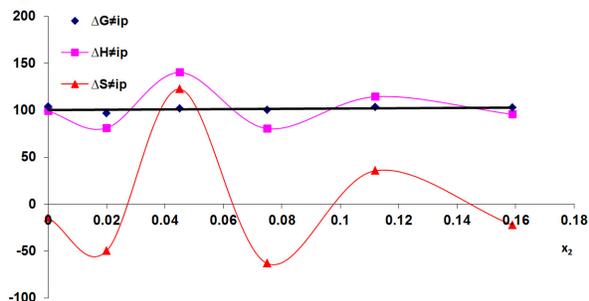

Figure 8. ΔG_{ip}^*, ΔH_{ip}^* and ΔS_{ip}^* versus x_2 for Malonate buffer at different solvent compositions.

Figure 9 shows the plots of ΔH_{ip}^* versus ΔS_{ip}^* for the ion-pair aquation reactions at different compositions of *tert*-butanol with an isokinetic temperature, $\beta=58$ ^{o}C, which lies within the temperature range studied (30-60 ^{o}C), this emphasizes the compensation effect. The true explanation of compensation effect lies in solute-solvent interactions, where the interaction between the solute and one of the solvent components, which is *tert*-butanol, is particularly strong. This will lower the enthalpy; it will also, by restricting the freedom of vibration and of rotation of the solvent molecules, will lower the entropy.
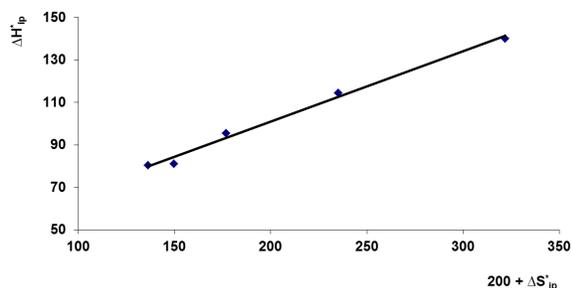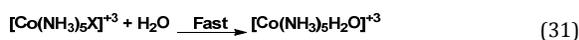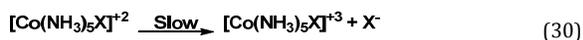

Figure 9. ΔH_{ip}^* versus ΔS_{ip}^* for Malonate buffer at different solvent compositions at 60 ^{o}C.

3.4. Variation of free energy of transfer with solvent composition

It has long been recognized that the solvolysis reactions of Co(III) complexes [25,26], proceed via the I_d mechanism [27,28] involving the rate-determining loss of the halide ion according to the following equations:

$$[Co(NH_3)_5X]^{+2} \xrightarrow{\text{Slow}} [Co(NH_3)_5X]^{+3} + X^- \quad (30)$$

$$[Co(NH_3)_5X]^{+3} + H_2O \xrightarrow{\text{Fast}} [Co(NH_3)_5H_2O]^{+3} \quad (31)$$

The extreme extension of Co-X bond in the transition state is revealed by a comparison of the volumes of activation with the overall volume changes for related Co(III) complexes. The situation affects the ions in the transition state to be independently solvated, which allows the application of a free energy cycle constructed by Wells [29], relating the process

initial state into transition state for the aquation of the six co-ordinated complex $[Co(NH_3)_5X]^{+2}$ to give five co-ordinated $[Co(NH_3)_5X]^{+3}$ intermediate together with the halide ion in the transition state in water (W) and in the mixed solvent (S) [29-30] according to the following scheme:

Initial state transition state
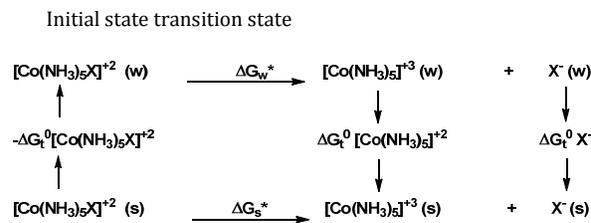
where ΔG_i^* is the activation free energy in the medium i (i = W for water and S for the mixed solvent). Equation (32) results from this cycle, where $\Delta G_t^0(i)$ is the free energy of transfer of species (i) between water and the mixed solvent.
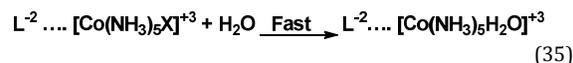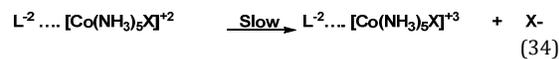
$$\Delta G_S^* - \Delta G_W^* = \Delta G_t^0[Co(NH_3)_5]^{+3} + \Delta G_t^0(X) - \Delta G_t^0[Co(NH_3)_5X]^{+2} \quad (32)$$

Converting free energies of activation, ΔG^*, into rate constant (32) can be rearranged to Equation (33):

$$2.303.R.T.Log\frac{K_w}{K_s} - \Delta G_t^0(X) = \Delta G_t^0[Co(NH_3)_5]^{+3} - \Delta G_t^0[Co(NH_3)_5X]^{+2} \quad (33)$$

which relates the rate constant with non-electrostatic component of the solvent mixture.

While applying the free energy cycle for the ion-pair effect on the aquation of the bromopentaamminecobalt(III) complex ion in the dicarboxylates media follow the following equations:

$$L^{-2} .... [Co(NH_3)_5X]^{+2} \xrightarrow{\text{Slow}} L^{-2} .... [Co(NH_3)_5X]^{+3} + X^- \quad (34)$$

$$L^{-2} .... [Co(NH_3)_5X]^{+3} + H_2O \xrightarrow{\text{Fast}} L^{-2} .... [Co(NH_3)_5H_2O]^{+3} \quad (35)$$

However, Equation (33) can be converted to Equation (36)

$$2.303.R.T.Log\frac{K_w}{K_{ip}} - \Delta G_t^0(X) = \Delta G_t^0(L^{-2}...[Co(NH_3)_5])^{+3} - \Delta G_t^0(L^{-2}...[Co(NH_3)_5X])^{+2} \quad (36)$$

Values of k_0 and k_{ip} at 25 °C were obtained from the interpolation of Arrhenius plot and values of $\Delta G_t^0(Br^-)$ were obtained from the literature [29], for *tert*-butanol-water mixtures with a range of co-solvent. Figure 10 depicts the variation of the values of the left hand side of the Equation (36) at 25 °C as a function of mole fraction of the co-solvent from which the differential solvating behavior of different malonate buffer for the initial and transition state is clearly evident. All the values on the left hand side of Equation (36) are negative as found for the aquation of a wide range of cobalt(III) complexes in a mixture of water with different co-solvents [31-33]. In all these cases, the effect of changing solvent structure on the pentacoordinatedcobalt cation in the transition state dominate the effect on the hexacoordinatedcobalt(III) cation in the initial state. Thus, these negative values in the left hand side of Equation (36) indicate that $[Co(NH_3)_5]^{+3}$ is more stable in *tert*-butanol-water in the presence of malonate buffer than $[Co(NH_3)_5Br]^{+2}$. Moreover, the presence of the malonate buffer in *tert*-butanol stabilizes the complex more than the free solvent. This is obvious from the more negativity of left hand side of the Equation (36) of malonate media and the free complex.
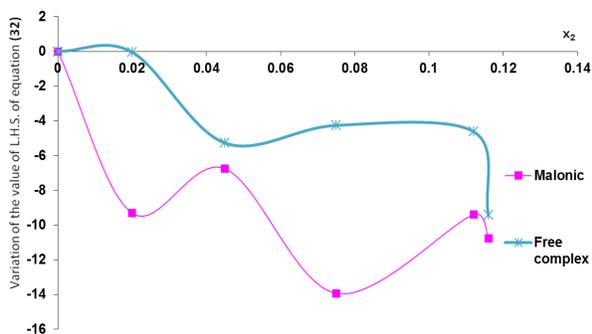
Figure 10. Variation of the value of L.H.S. of equation (36) versus the mole fraction x_2 at 25 °C.

4. Conclusion

In conclusion from all the above discussion, the aquation reaction was accelerated in the presence of malonate buffer due to the formation of ion-pair between the complex cation and the added anion. The plot of log k_{ip} versus the dielectric constant is non linear which means that the internal structure of the medium is suffered from serious changes on the progress addition of *tert*-butanol to water. As well as, the non linearity of log k_{ip} versus Log [H_2O] and the Grunwald-Winstein y-values confirms the differential effect of solvent structures between the initial and the transition states. From the extrathermodynamic correlations, there is marked effect of both solute-solvent and solvent-solvent interactions on the ion-pair formation and aquation reaction. The free energy of activation ΔG_{ip}^* is more or less linearly varied with the mole fraction of tert-butanol indicating of the presence of compensation effect between ΔH_{ip}^* and ΔS_{ip}^*. From the negative values of left hand side of Equation (32), we can conclude that the ions in the transition are more stable than the initial state.

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