

Kinetic studies of ion-pairing effects on the aquation of chloropentaammine cobalt(III) complex in different dicarboxylate media at 30% of *tert*-butanol

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ABSTRACT

The study of the kinetic aquation of chloropentaammine cobalt(III) ion in the presence of different types of dicarboxylate solutions (Malonate, malate, tartarate and succinate), in mixed solvent media of water with *tert*-butanol (30%, *v:v*) is investigated spectrophotometrically at different temperatures (30-60 °C) in the light of the effects of ion-pairing on reaction rates and mechanism. Comparison of the k_{ip} (Rate constant of ion-pairing) values with respect of different buffers (Malonate, malate, tartarate and succinate) at 30% of *tert*-butanol is introduced. Examination of the linear free energy relationship (LFER) at the mentioned conditions will lead to diagnose the mechanism. The free energy of activation ΔG^*_{ip} is more or less linearly varied among the studied dicarboxylate ion-pairing ligands indicating the presence of compensation effect between ΔH^*_{ip} and ΔS^*_{ip} .

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1. Introduction

Cobalt(III) complexes have attracted considerable attention, notably because of their biological activity. Cobalt(III) complexes with tetradentate aliphatic Schiff bases, containing also members of the vitamin B series or their analogues, as axial ligands have been synthesized as potential antitumor agent [1]. Also, the electrochemical studies of cobalt(III) in the form of its *tris*(methylpyridyl) amine complex showed that the reduction potential of the complex is suitable for it to be bio-reductively activated at hypoxic tumor sites [2].

Carboxylic acids are found at mg/L concentrations in sedimentary basin fluids, but are typically present in surface water at mg/L concentrations where they can account for 5 to 8% of the dissolved organic carbon. In spite of their variable concentrations in natural waters, their abilities to form complexes with metal cations have led to numerous studies of their roles in mineral dissolution, secondary porosity enhancement, trace element mobility, ore deposition, petroleum formation and migration, trace element bioavailability and toxicity. By forming complexes with metal cations on mineral surface or by decreasing the pH of soil solutions, carboxylic acids are capable of increasing dissolution of aluminosilicates,

carbonates, quartz and barite port in high-temperature ore-forming fluids, where metal-organic complexes can be highly associated as a result of high temperature [3-5].

Several works investigated the kinetics of aquation of halopentaammine cobalt(III) in different media [6-12]. It is known that the halopentaammine cobalt(III) complexes aquated by an essentially dissociative process. Stronger ionic interactions result in contact ion-pairing, where no solvent separates the ion-pair. The strength of ion-pairing is primarily dependent on the charge to size ratio of the ions and not on any specific chemical interactions [13].

The purpose of the introduced work is to study the aquation of chloropentaammine cobalt(III) perchlorate in malonate, succinate, malate and tartarate solutions (0.008-0.04 mol/L of dicarboxylic acid neutralized by 80% of Na_2CO_3) containing 30% (*v:v*) *tert*-butanol at different temperatures in an attempt to determine the 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

Table 1. Values of rate constants ($k_0 \times 10^6$) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in the absence of dicarboxylate ion-pairing *tert*-butanol (30%) at different temperatures.

T (°C)	30	35	40	50	60
$k_0 \times 10^6$ (1/sec)	0.51	1.80	3.56	30.40	37.80

Table 2. Values of rate constants ($k_{\text{obs}} \times 10^6$ (1/sec)) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in malate media (m_1) containing *tert*-butanol (30%) at different temperatures.

m_1 (mol/L)	T (°C)				
	30	35	40	50	60
0.008	0.78	3.39	14.47	39.95	61.20
0.016	0.74	3.43	13.83	38.32	57.61
0.024	0.76	3.71	11.35	21.46	55.97
0.032	0.78	3.59	6.86	11.38	54.80
0.040	0.65	3.90	7.31	10.43	32.89

Table 3. Values of rate constants ($k_{\text{obs}} \times 10^6$ (1/sec)) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in malonate media (m_1) containing *tert*-butanol (30%) at different temperatures.

m_1 (mol/L)	T (°C)				
	30	35	40	50	60
0.008	2.65	5.02	6.82	31.36	50.24
0.016	2.83	4.27	7.51	29.67	55.52
0.024	1.69	2.20	7.24	32.49	53.84
0.032	0.87	5.83	7.42	29.68	51.65
0.040	1.26	5.09	5.26	40.33	56.27

Table 4. Values of rate constants ($k_{\text{obs}} \times 10^6$ (1/sec)) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in tartrate media (m_1) containing *tert*-butanol (30%) at different temperatures.

m_1 (mol/L)	T (°C)				
	30	35	40	50	60
0.008	0.57	4.13	5.84	18.60	47.23
0.016	2.24	3.25	6.52	17.58	45.90
0.024	2.45	2.95	4.22	16.14	44.42
0.032	0.74	2.79	20.74	35.29	67.13
0.040	0.83	3.33	12.06	26.70	60.80

Table 5. Values of rate constants ($k_{\text{obs}} \times 10^6$ (1/sec)) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in succinate media (m_1) containing *tert*-butanol (30%) at different temperatures.

m_1 (mol/L)	T (°C)		
	30	35	40
0.008	1.51	2.01	5.34
0.016	1.05	1.51	2.31
0.024	0.85	2.20	3.20
0.032	1.27	3.09	3.02
0.040	1.35	2.31	3.93

Cobalt(II) carbonate, ammonia, malonic acid, succinic acid, tartaric acid, malic acid, sodium carbonate and *tert*-butanol were purchased from Fluka Chemika. Hydrogen peroxide was purchased from Riedel-de Haën. Hydrochloric acid was purchased from Chemical Management Consulting. Perchloric acid was purchased from Merck. The chloropentaammine cobalt(III) perchlorate complex was prepared by using the method of Hynes [14].

2.2. Procedure

The rate of aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ complex was followed spectrophotometrically by using Unicam Helios Alpha and Beta spectrophotometer at $\lambda = 240$ nm, in 30% (v:v) *tert*-butanol in different dicarboxylate media (Malonate, succinate, malate and tartrate) (0.008-0.040 mol/L at 30-60 °C). Knowing that, the buffer solution was prepared from 0.1 M of the dicarboxylic acid and 0.08 M of sodium carbonate. The spectrophotometer was fitted with thermostated cell holders, heated by water circulating from a Heto HMT 200 thermostat.

3. Results and discussion

The observed first order rate constant in the presence of dicarboxylate buffers for different temperatures in 30% (v:v) *tert*-butanol were computed from the slopes of the good linear least squared first order plots of $\log (A_t - A_\infty)$ against time depending on the first order Equation (1) [15]. Where A_t is the

absorbance at different time and A_∞ is the absorbance at the infinite time.

$$\ln (a_0/a_0 - x) = k \times t \quad (1)$$

The observed rate constants (k_{obs}) are collected in Tables 1-5. The ion-pair rate coefficient (k_{ip}) was calculated according to the following Wyatt and Davis equation [16].

$$k_{\text{obs}, m_3} = k_0 \times [\text{CpX}^{2+}] + k_{\text{ip}} \times [\text{CpXL}] \quad (2)$$

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; $[\text{CpX}^{2+}]$, the free complex ion concentration and $[\text{CpXL}]$, the ion-pair concentration.

$[\text{CpXL}]$ was calculated with the aid of the following Equations:



Table 6. Calculated values of rate constants ($k_{ip} \times 10^5$, 1/sec) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in dicarboxylate buffer containing 30% of *tert*-butanol at different temperatures.

T (°C)	Malate	Malonate	Tartrate	Succinate
30	0.38	0.835	0.30	0.21
35	1.95	1.23	0.42	0.22
40	6.02	1.32	0.925	0.33
50	8.49	3.14	2.30	
60	21.10	7.68	4.95	

Table 7. Values of the thermodynamic parameters: Enthalpy of activation ΔH_{ip}^* , entropy of activation ΔS_{ip}^* and Gibbs of free energy of activation ΔG_{ip}^* of the ion-pairing aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in different buffers containing 30% of *tert*-butanol at 40 °C.

T (°C)	Buffer	ΔH_{ip}^* (kJ/mole)	ΔS_{ip}^* (J/K.mole)	ΔG_{ip}^* (kJ/mole)
40	malate	98.25	-18.74	104.11
40	malonate	52.49	-168.50	105.22
40	tartrate	72.48	-112.11	107.57
40	succinate	22.18	-280.11	109.86

Where;

$$K_D = [\text{CpX}^{2+}][\text{L}^{2-}]\gamma_2^2 / [\text{CpXL}] \quad (7)$$

(L^{2-} represents the dicarboxylate anion)

$$K_1 = [\text{H}^+][\text{HL}^-] \gamma_1^2 / [\text{H}_2\text{L}] \quad (8)$$

$$K_2 = [\text{H}^+][\text{L}^{2-}] \gamma_2 / [\text{HL}^-] \quad (9)$$

$$K_{\text{NaL}^-} = [\text{Na}^+][\text{L}^{2-}] \gamma_2 / [\text{NaL}^-] \quad (10)$$

$$\text{Log } \gamma_1 = -A \times (I^{1/2} / (1 + 1.3 \times I^{1/2}) - 0.3 \times I) \quad (11)$$

(Debye-Hückel equation) ($\text{Log } \gamma_2 = 4 \text{ Log } \gamma_1$)

I is the ionic strength γ_1 and γ_2 are the activity coefficients of the univalent and divalent ions, respectively.

$$I = 0.5 \times ([\text{H}^+] + [\text{HL}^-] + 4 \times [\text{L}^{2-}] + 4 \times [\text{CpX}^{2+}] + 2 \times m_3 + [\text{Na}^+] + [\text{NaL}^{2-}]) \quad (12)$$

$$m_1 = [\text{H}_2\text{L}] + [\text{HL}^-] + [\text{CpXL}] + [\text{NaL}^-] \quad (13)$$

$$m_3 = [\text{CpX}^{2+}] + [\text{CpXL}] \quad (14)$$

The principle of calculations performed by computer programs can be summarized as: for the first cycle $[\text{H}^+] = 0$, $[\text{CpXL}] = 0$, $[\text{NaL}^-] = 0$, $[\text{CpX}^{2+}] = m_3 - [\text{CpXL}]$, $[\text{HL}^-] = 0.5 \times m_2$, $[\text{H}_2\text{L}] = 0.3 \times m_1$, $[\text{L}^{2-}] = m_1 - [\text{HL}^-] - [\text{CpXL}] - [\text{NaL}^-] - [\text{H}_2\text{L}]$ and $[\text{Na}^+] = 2 \times m_2 - [\text{NaL}^-]$. Where, m_2 is the concentration of sodium carbonate.

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

$$[\text{H}^+] = K_2 [\text{HL}^-] / [\text{L}^{2-}] \gamma_2 \quad (15)$$

$$[\text{H}_2\text{L}] = [\text{HL}^-][\text{H}^+] \gamma_1^2 / K_1 \quad (16)$$

$$[\text{HL}^-] = 2 \times m_1 - 2 \times m_2 - 2 \times [\text{H}_2\text{L}] - [\text{H}^+] \quad (17)$$

$$[\text{L}^{2-}] = m_1 - [\text{HL}^-] - [\text{H}_2\text{L}] - [\text{CpXL}] - [\text{NaL}^-] \quad (18)$$

$$[\text{NaL}^-] = [\text{Na}^+][\text{L}^{2-}] \gamma_2 / K_{\text{NaL}^-} \quad (19)$$

$$[\text{CpXL}] = m_3 / [(K_D / \gamma_2^2 \times [\text{L}^{2-}]) + 1] \quad (20)$$

$$[\text{CpX}^{2+}] = m_3 - [\text{CpXL}] \quad (21)$$

then I , γ_1 and γ_2 recalculated again. These steps of calculations were repeated many times until the difference between two successive values of $[\text{CpXL}]$ becomes equal to or less than 1×10^{-7} .

The calculated average values of k_{ip} in dicarboxylate buffer containing 30% of *tert*-butanol at different temperatures are collected in Table 6.

3.1. Variation of ion-pair coefficients (k_{ip}) with different buffers

Various studies [17] found that the rate of aquation of chloropentaammine chromium(III) ion is accelerated by nitrate, sulphate, malonate, tartrate and phthalate ions. These effects were attributed to the more reactive ion-pairs. These studies clearly show the ion-pairs formed between some bivalent anions and halopentaammine cobalt(III) or chromium(III) cations undergo aquation at a faster rate as compared to the free cations. Thus, by comparing k_{obs} of all buffers with respect to k_0 (in the absence of buffer) at 30% of *tert*-butanol (see Tables 1-5), it was seen that k_{obs} values are greater than the k_0 values. The rate of the acid hydrolysis of chloropentaammine cobalt(III) ion had been shown to be independent of hydrogen ion concentration below $\text{pH} = 7$ [18]. For that reason, the values of ion-pair rate constant k_{ip} are approximately the same at different concentration of buffers. Table 6 shows the average values of k_{ip} for the different buffers at different temperatures containing 30% of *tert*-butanol. By comparing the k_{ip} values with respect to different buffers, it was seen that the values of k_{ip} are of decreasing order: k_{ip} malonate > k_{ip} tartrate > k_{ip} succinate at different temperature. Knowing that $\text{p}K_1$ succinate > $\text{p}K_1$ tartrate > $\text{p}K_1$ malate > $\text{p}K_1$ malonate. This means that malonate will dissociate more than the other buffers causing more anions of malonate in solution, thus helping in the formation of ion-pair. Furthermore, the solute-solvent and the solvent-solvent interactions must be considered resulting from the presence of hydroxyl groups in both solvent components (water and *tert*-butanol) and the carbonyl oxygens group in the malate, malonate, tartrate and succinate buffers besides the hydroxyl groups in tartrate and malate in the formed ion-pairs. So, *tert*-butanol has special effect on the formation of ion-pair. This fact was also proven in previous studies [19-21].

3.2. Thermodynamic parameters of the ion-pair aquation reaction

The thermodynamic parameters of the activated complex at 40 °C were collected in Table 7. A useful comparison can be made with ΔG_{ip}^* values among the studied dicarboxylates. The most positive values of ΔG_{ip}^* were found for succinic buffer as shown in Table 7. The trend of stability of ion-pairs is based on the ring size formed between the complex cation and dicarboxylate anion in which the stability increases with decreasing ring size [22]. Accordingly, malonate is the most stable one. The stability of tartrate and malate ion-pairs is higher than succinate (same chain length) due to the presence

of hydroxyl groups which through interactions with the complex cation increases the stability of ion-pair. Furthermore, the electrostatic action transmitted through solvent molecules (field effect) also governs these solute-solvent interactions and their thermodynamics results. The charged anions (HL^- , L^{2-}) of these acids impose order on the surrounding solvent molecules, which interferes with internal rotation of the alkyl chain of the acid [22].

Any explanation of the effect of structural or medium changes on the rate or equilibrium of chemical reactions must in some way reflect the inherent complexity of the mechanism of a chemical reaction. When the explanation is given in terms of similar effects in a model reaction, the quantities compared are thermodynamic, usually free energies, enthalpies, or entropies. The simple relationships often found among such quantities are not part of the formal thermodynamics but they are called extrathermodynamic relationships. Although the thermodynamics do not give identified detailed microscopic mechanisms, however, the mathematical form of extrathermodynamic relationship gives valuable information about the microscopic mechanism. Thus, examining the linear free energy relationship (LFER) among the studied dicarboxylate series ($\Delta G_{ip}^* - \Delta G_{ass}^0$), it will lead to diagnose the mechanism [23] by determining the extent of bond formation or breakage in the transition state.

The plot of ΔG_{ip}^* against ΔG_{ass}^0 is shown in Figure 1. The plot is linear due to the following correlation of Equation (22):

$$\Delta G_{ip}^* = a \times \Delta G_{ass}^0 + b \quad (22)$$

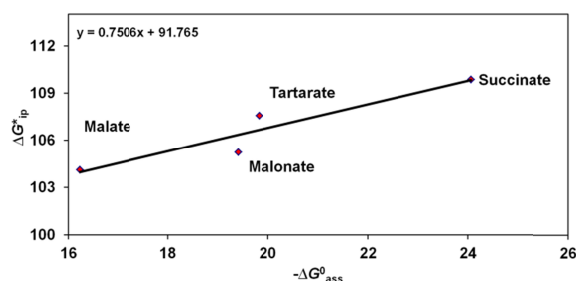


Figure 1. ΔG_{ip}^* versus ΔG_{ass}^0 for the different buffers containing 30% of *tert*-butanol for $[Co(NH_3)_5Cl]^{2+}$ at 40 °C.

This permits a suitable medium for ion association. Knowing that, a and b are variables for the solute-solvent interaction. Besides the correlation of ΔG_{ip}^* and ΔG_{ass}^0 , similar attempts are made for correlating ΔG_{ip}^* with either ΔG_1^0 or ΔG_2^0 . The plot of ΔG_{ip}^* against ΔG_1^0 among the studied dicarboxylates at 30% of *tert*-butanol is also linear as it is shown in Figure 2. But the plot of ΔG_{ip}^* against ΔG_2^0 is nonlinear as it is shown in Figure 3. This non-linear correlation arises from the higher selective solvation of the free dicarboxylate anion leading to a complex pattern of solute-solvent interaction.

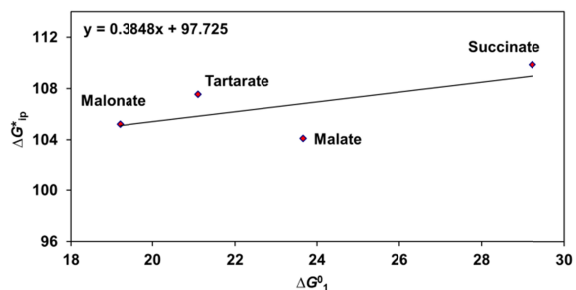


Figure 2. ΔG_{ip}^* versus ΔG_1^0 for the different buffers containing 30% of *tert*-butanol for $[Co(NH_3)_5Cl]^{2+}$ at 40 °C.

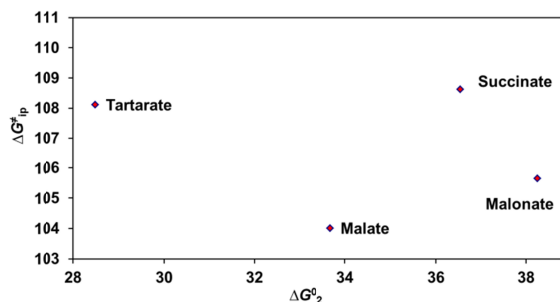


Figure 3. ΔG_{ip}^* versus ΔG_2^0 for the different buffers containing 30% of *tert*-butanol for $[Co(NH_3)_5Cl]^{2+}$ at 40 °C.

Similar to (LFER), ΔH_{ip}^* is correlated with ΔH_{ass}^0 to give the following Equation (23):

$$\Delta H_{ip}^* = c \times \Delta H_{ass}^0 + d \quad (23)$$

Other correlations are done to ΔH_{ip}^* with ΔH_1^0 and ΔH_2^0 , where they are found to obey Equation (23).

Also, the plot of ΔS_{ip}^* versus ΔS_{ass}^0 of the dicarboxylate ligand series is found to be linear. This relationship takes the form of Equation (24):

$$\Delta S_{ip}^* = e \times \Delta S_{ass}^0 + f \quad (24)$$

The obtained link suggests that both entropies of activation ΔS_{ip}^* and association ΔS_{ass}^0 are largely charge-controlled. Moreover, the parallelism between ΔS_{ip}^* and ΔS_{ass}^0 for the different dicarboxylates is probably related to ion solvation, where the controlled factor is the reorientation of the hydration shell for the free complex ion and ion-pair. The position taken by every dicarboxylate buffer in the above linear correlations, depends on its reactivity toward the ion-pair formation which differs from one dicarboxylate to another primarily because of the electrostatic action on the dicarboxylate groups transmitted through ($-CH_2-$) groups and the hydroxyl groups [24].

3.3. Isokinetic relationship

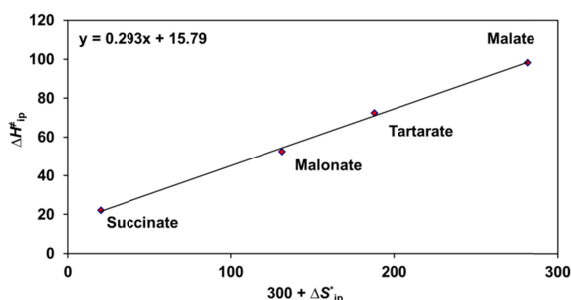
Plots of enthalpies of activation versus entropies of activation often form straight line. Several standard chemistry texts [25,26] treat these linear plots as authentic representation of an extrathermodynamic relationship, which is sometimes called the isokinetic effect, enthalpy-entropy compensation effect. The isokinetic temperature can be determined from the slope $\times 1000$ of the linear plots of ΔH_{ip}^* versus ΔS_{ip}^* . Enthalpy-entropy diagrams for mixed solvents are often interpreted by assuming that solvent-solute interactions are of dominant importance where the interaction between the solute and one of the solvent components, which is *tert*-butanol, is particularly strong. Then, the enthalpy and the entropy will both tend to ΔH_{ip}^* and ΔS_{ip}^* led to only small changes in ΔG_{ip}^* be linear functions. Figure 4 shows the plot of ΔH_{ip}^* versus ΔS_{ip}^* for the ion-pair aquation reactions in different dicarboxylate media at fixed composition.

Thus the computed value of the isokinetic temperature is 293 K. This means that the compensation effect must be born in mind. The true explanation of compensation effect lies in terms of solvent-solute interactions. Any effect for example, leads to stronger binding between a solute molecule and the solvent molecules will lower the enthalpy; it will also, by restricting the freedom of vibration and of rotation of the solvent molecules, lower the entropy.

Table 8. Values of ligand concentration C_L (mol/L) for the aquation of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in different concentrations m_1 of dicarboxylate buffer containing 30% of *tert*-butanol at 40 °C.

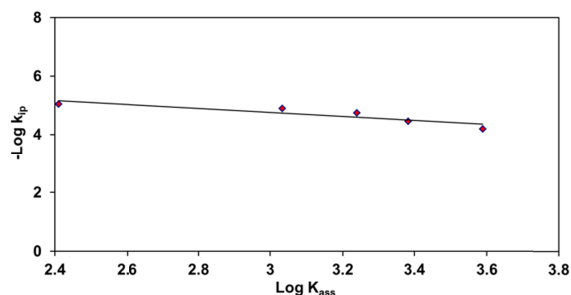
m_1	Malate	Malonate	Tartrate	Succinate
0.008	0.00474529	0.00464804	0.00480857	0.00475858
0.016	0.00946801	0.00929403	0.00964962	0.00962388
0.024	0.01416970	0.01390796	0.01448190	0.01448540
0.032	0.01885338	0.01849560	0.01930297	0.01933650
0.040	0.02351778	0.02305878	0.02411015	0.02417636

Application of more exact theories to these effects leads to the result that they will generally give rise to a fairly exact compensation between ΔH_{ip}^* and $T \times \Delta S_{ip}^*$, and therefore to a very small effect on ΔG_{ip}^* which is the case of the present investigation.

**Figure 4.** ΔH_{ip}^* versus ΔS_{ip}^* for the different buffers containing 30% of *tert*-butanol for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at 40 °C.

3.4. Correlation of $\log k_{ip}$ with $\log K_{ass}$, $\log K_1$ and $\log K_2$

All the above correlations are performed at constant temperature which is 313 K. It is now necessary to examine the above correlations among the studied temperatures for each dicarboxylate buffers at fixed solvent composition. $\log k_{ip}$ at different temperature is used instead of ΔG_{ip}^* , $\log K_1$ instead of ΔG_1^0 , $\log K_2$ instead of ΔG_2^0 and $\log K_{ass}$ instead of ΔG_{ass}^0 . Some examples are chosen to show such correlations Figures 5-7. It is evident from the plots that these correlations are linear. The obtained results indicate that the parallelism between each pair of thermodynamic functions among the different studied temperatures for each dicarboxylate buffer at fixed composition support that these reactions sharing the same mechanism and same LFER behaviour also at different temperatures.

**Figure 5.** $\log k_{ip}$ versus $\log K_{ass}$ of malonate containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at different temperatures.

3.5. Empirical correlation of k_{obs} with dicarboxylate anion concentration

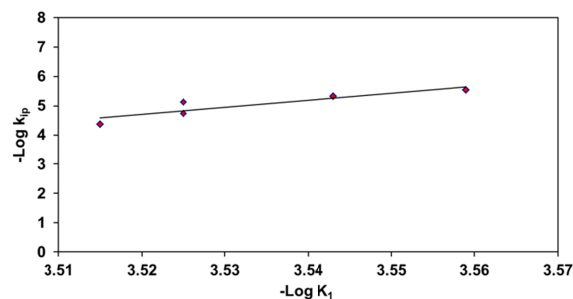
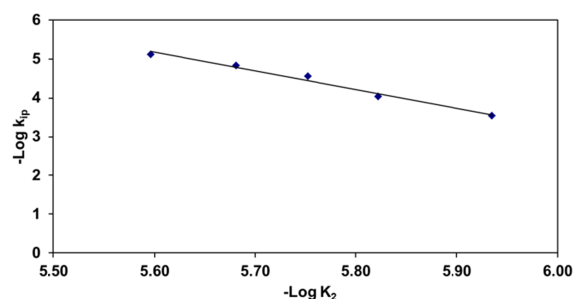
The aim of this part is to pay an effort in order to form a new empirical correlation between the different parameters which are influencing the rate of aquation in aqueous

dicarboxylate solutions and that containing *tert*-butanol. Garrick [27] expressed his results in terms of Equation (25):

$$K_{obs} = k_0 + k_c \times C_L \quad (25)$$

where k_{obs} is the observed pseudo-unimolecular rate constant, k_0 its value is the absence of L, k_c is the catalytic coefficient and C_L is the stoichiometric concentration of the univalent ligand (collected in Table 8). Jones, Harris and Wallace [28] found that the plots of k_{obs} against C_L of univalent ligand were linear and extrapolated to a common k_0 at $C_L = 0$ while for divalent ligands the plots are nonlinear. Thus, it was concluded that the appropriate rate law is:

$$\text{Rate} = C_1 (k_0 + k_c K_A C_L) / (1 + K_A C_L) \quad (26)$$

**Figure 6.** $\log k_{ip}$ versus $\log K_1$ of tartrate buffer containing 30% of *tert*-butanol for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at different temperatures.**Figure 7.** $\log k_{ip}$ versus $\log K_2$ of malate buffer containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at different temperatures.

In the present investigation it is now necessary to examine the possible empirical correlations in the dicarboxylate solutions containing 30% of *tert*-butanol which assist such correlations rather than the pure aqueous dicarboxylates medium where the added *tert*-butanol lowered the dielectric constant and hence assisted the ion-association process. Figures 8 and 9 show such plots which appear smooth.

Now, it is necessary to correlate the observed rate constant (k_{obs}) with the free ligand concentration C_L . Different attempts were tested and one of them was only valid in which the plots of $1/(k_{obs}-k_0)$ versus $1/C_L$ give a straight line with a positive slope and positive intercept. Some examples are shown on Figures 10 and 11. The linearity obtained from these plots leads to the following empirical correlation:

$$\frac{1}{(k_{\text{obs}} - k_0)} = a + \frac{b}{[L]} \quad (27)$$

Where a and b are empirical constants and Equation (27) can take another form:

$$k_{\text{obs}} = \frac{k_0 + \left[\frac{a}{b} + \frac{1}{b} \right] [L]}{1 + \left(\frac{a}{b} \right) [L]} \quad (28)$$

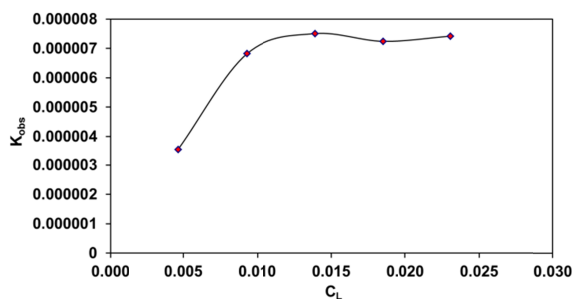


Figure 8. k_{obs} versus C_L of malonate buffer containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at 40 °C.

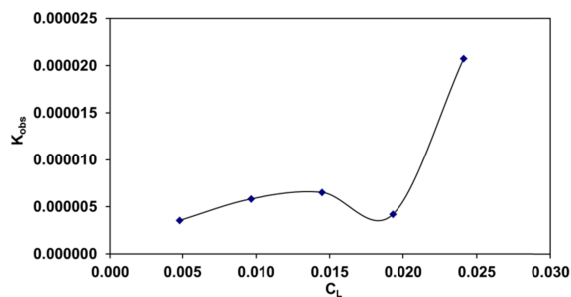


Figure 9. k_{obs} versus C_L of tartarate buffer containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at 40 °C.

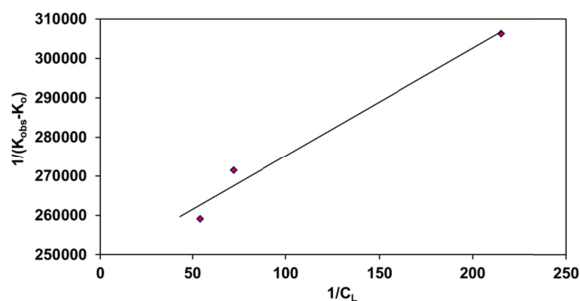


Figure 10. $1/(k_{\text{obs}} - k_0)$ versus $1/C_L$ of malonate buffer containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at 40 °C.

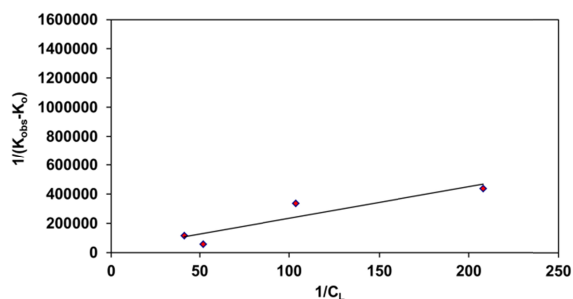


Figure 11. $1/(k_{\text{obs}} - k_0)$ versus $1/C_L$ of tartarate buffer containing 30% of *tert*-butanol buffer for $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ at 40 °C.

4. Conclusions

We have noted, the rate of aquation reaction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ complex is increased in the presence of dicarboxylate buffer due to the formation of ion-pair between the complex cation and the added anion. Where, the trend of stability of ion-pairs is based on the ring size formed between the complex cation and dicarboxylate anion in which the stability increases with decreasing ring size. From the extrathermodynamic correlations, there is marked effect of both solute-solvent and solvent-solvent interactions on the ion-pair formation and aquation reaction. These facts are also noticed at different temperatures. 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}^* .

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