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Comparison of the leaving groups during the study of the aquation of halopentaammine cobalt(III) complex in tartarate at different percentage of *tert*-butanol

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RESEARCH ARTICLE

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ABSTRACT

The experimental kinetic study of aquation for both complexes bromopentaammine cobalt(III) and chloropentaammine cobalt(III) ions in the presence of tartarate solution in mixed solvent media of water with *tert*-butanol (10-50%, *v*:*v*) was examined spectrophotometrically at different temperatures (30-60 °C) by comparing the special effects of the leaving group of chloro and bromo on the rate constant of aquation. Comparison of k_{ip} (rate constant of ion-pairing) for both complexes and show the non-linear plots of log (k_{ip}) ion-pair rate constants against the reciprocal of the dielectric constant D. The thermodynamic analyses of the kinetic data for both complexes 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 excessive change of ΔH_{ip}* and ΔS_{ip}* with the mole fraction of the co-solvent can be recognized to the change of the physical properties of the solvent-water mixture with the solvent structure. Undersized changes in ΔG_{ip}* with the mole fraction of the co-solvent was found, representing a compensating effects between ΔH_{ip}* and ΔS_{ip}*.

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1. Introduction

The chemistry of metal complexes has been studied quite extensively both in solid state and in solution (both aqueous and non-aqueous). However, certain aspects of solution chemistry of metal complex will be reviewed in some details for the sake of brevity and resemblance. A lot of theoretical and experimental discussions on the reactions of coordination complexes in solutions were studied [1-5].

Several achievements were investigated on the kinetics of aquation of halopentaammine cobalt(III) in different media [6-12]. It is well 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 relative order "bond breaking is more important than bond making" was characteristic of the aquation reactions of Co(III) ammine-halide complexes although there was some indirect evidence for some degree of bond making by the water molecule [14-16].

The aim of the introduced work is to compare between the two leaving group of the aquation of halopentaammine cobalt(III) perchlorate in tartarate solutions (0.008-0.040 mol/L of dicarboxylic acid neutralized by 80% of Na_2CO_3) containing 10-50% (*v*:*v*) *tert*-butanol at different temperatures as well as to determine the thermodynamic parameters of activation in order to characterize further information about the solute-solvent interaction.

2. Experimental

2.1. Reagents

Cobalt(II) carbonate, ammonia, hydrobromic acid 48%, tartaric acid, sodium carbonate and *tert*-butanol were purchased from Fluka Chemika.

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Table 1. Values of rate constants ($k_o \times 10^6$ in sec^{-1}) for the aquation of $[Co(NH_3)_5Br]^{2+}$ in *tert*-butanol (10-50%) at different temperatures in the absence of tartarate ion-pairing ligand.

Temperature (°C)	*tert*-Butanol %				
	10	**20**	**30**	**40**	**50**
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

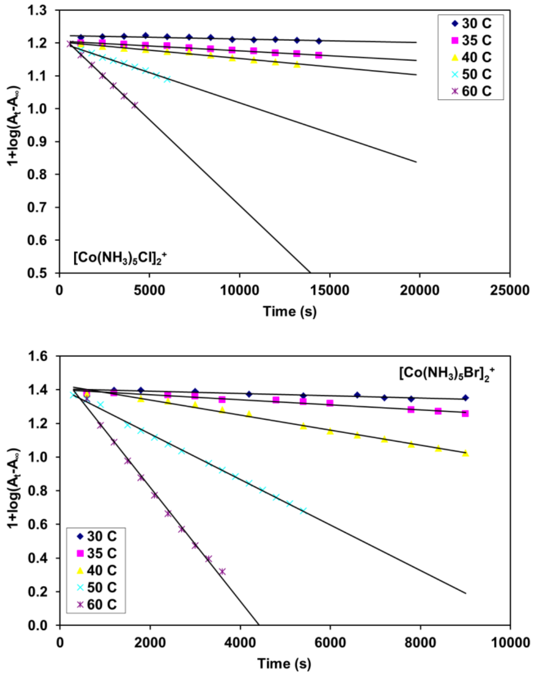

Figure 1. By comparing the plots of log (A_t-A_∞) against time of aquation of bromopentaammine cobalt(III) ion with chloropentaammine cobalt(III) ion.

Hydrogen peroxide was purchased from Riedel-de Haën. Hydrochloric acid was purchased from Chemical Management Consulting. Perchloric acid was purchased from Merck. The tartaric acid was recrystallized and dried. Pure co-solvent *tert*-butanol was further redistilled. Sodium carbonate was dried at 300 °C for three hours. The chloropentaammine cobalt(III) perchlorate and bromopenta- ammine cobalt(III) perchlorate complexes were prepared by using the method of Hynes [17].

2.2. Procedure

The rate of aquation was followed spectrophotometrically by using Unicam Helios Alpha and Beta spectrophotometer at λ = 240 nm for $[Co(NH_3)_5Cl](ClO_4)_2$ complex and at λ = 250 nm for $[Co(NH_3)_5Br](ClO_4)_2$ complex, in different percentage by volume of *tert*-butanol in buffer solution (0.008-0.040 mol/L) at 30-60 °C. Knowing that, the buffer solution was prepared from 0.1 M of the tartaric acid and 0.08 M of sodium carbonate. The spectrophotometer was fitted with thermo-stated 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 tartarate media in different percentage (*v*:*v*) of *tert*-butanol at different temperatures were computed from the slopes of the good linear least squared first order plots of log (A_t-A_∞) against time [18] and some examples of the plots are shown in Figure 1. A_∞, absorbance at infinite time, is the absorbance of aquapentaammine cobalt(III) perchlorate at under the same experimental conditions. A_t is the absorbance at different time during the aquation study of the halopentaammine cobalt(III) complex. The observed rate constants for both complexes are collected in Tables 1-4.

The ion-pair rate coefficient (k_{ip}) was calculated according to the following Wyatt and Davis equation [19].

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

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,

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

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

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

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

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

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

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

Table 2. Values of rate constants ($k_{obs}\times10^{6}$in sec^{-1}) for the aquation of $[Co(NH_3)_5Br]^{2+}$ in tartrate media (m_1) containing *tert*-butanol at different temperatures.

***tert*-Butanol (%)**	**m_1 (mol/L)**	**Temperature (°C)**				
		30	**35**	**40**	**50**	**60**
10	0.016	6.17	10.03	18.53	97.48	288.35
	0.024	0.49	13.76	27.14	115.42	362.02
	0.032	8.46	17.62	30.34	118.43	300.26
	0.040	9.85	15.28	38.34	118.70	285.67
20	0.008	4.07	9.46	26.83	81.35	264.50
	0.016	3.78	10.10	28.90	114.27	299.30
	0.024	3.56	10.68	27.25	121.25	260.70
	0.032	7.67	21.17	34.66	139.01	283.14
	0.040	6.13	17.82	35.16	95.95	286.22
30	0.008	2.81	7.76	16.82	93.63	250.30
	0.016	3.00	8.22	29.65	88.62	237.70
	0.024	1.24	7.396	17.89	88.33	224.20
	0.032	2.10	10.02	38.92	110.83	295.60
	0.040	0.76	25.20	48.92	167.95	418.20
40	0.008	7.99	8.34	42.32	115.40	393.40
	0.016	10.00	14.86	42.52	128.63	434.30
	0.024	10.59	11.46	35.69	155.63	306.90
	0.032	6.90	14.98	44.75	135.37	338.50
	0.040	10.60	13.15	45.61	139.83	379.99
50	0.008	5.63	15.96	47.70	157.06	483.70
	0.016	6.63	17.49	50.36	113.30	426.70
	0.024	10.28	28.76	38.53	176.80	473.20
	0.032	7.37	35.70	58.28	178.00	496.20
	0.040	8.22	31.17	52.53	185.80	504.80

Table 3. Values of rate constants ($k_{obs}\times10^{6}$ in sec^{-1}) for the aquation of $[Co(NH_3)_5Cl]^{2+}$ in *tert*-butanol (10-50%) at different temperatures in the absence of tartrate media.

Temperature (°C)	***tert*-Butanol %**				
	10	**20**	**30**	**40**	**50**
30	0.25	0.16	0.51	0.68	0.62
35	1.82	2.78	1.80	2.79	0.694
40	5.61	3.67	3.56	3.10	2.39
50	17.90	17.90	30.40	5.12	9.03
60	53.60	50.80	37.80	31.70	38.40

Table 4. Values of rate constants ($k_{obs}\times10^{6}$in sec^{-1}) for the aquation of $[Co(NH_3)_5Cl]^{2+}$ in tartrate media (m_1) containing *tert*-butanol at different temperatures.

***tert*-Butanol (%)**	**m_1 (mol/L)**	**Temperature (°C)**				
		30	**35**	**40**	**50**	**60**
10	0.008	1.09	2.93	5.05	18.39	52.10
	0.016	1.20	2.62	4.86	19.44	59.46
	0.024	1.90	3.08	5.28	21.90	42.14
	0.032	2.59	3.60	5.16	28.38	74.72
	0.040	0.70	3.02	9.05	20.68	71.13
20	0.008	2.33	2.74	8.45	20.47	52.27
	0.016	1.85	2.94	5.16	14.77	54.71
	0.024	1.69	3.19	6.42	23.23	58.21
	0.032	1.47	1.98	6.84	27.36	52.42
	0.040	0.55	2.22	6.24	20.87	52.34
30	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
40	0.008	1.99	2.77	5.70	29.27	58.14
	0.016	1.89	4.49	6.58	21.51	58.81
	0.024	2.29	5.34	6.45	22.35	60.44
	0.032	1.13	3.85	7.51	17.94	58.07
	0.040	0.22	4.19	6.88	20.95	61.20
50	0.008	1.51	3.03	7.20	21.29	64.30
	0.016	1.83	5.50	7.66	23.24	61.77
	0.024	1.37	3.86	7.92	23.87	61.01
	0.032	1.79	4.65	5.50	29.71	56.49
	0.040	1.97	4.58	8.80	28.76	57.83

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

$$\text{Log } \gamma_i = -A(I^{1/2}/(1+1.3\ I^{1/2})-0.3I) \text{ (Debye-Hückel equation) } (\log \gamma_2 = 4 \log \gamma_1) \qquad (10)$$

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

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

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

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

The principle of calculations performed by computer programs can be summarized as: for the first cycle $[H^+] = 0$, $[CpXL] = 0$, $[NaL^-] = 0$, $[CpX^{2+}] = m_3 - [CpXL]$, $[HL^-] = 0.5\ m_2$, $[H_2L] = 0.3\ m_1$, $[L^{2-}] = m_1 - [HL^-] - [CpXL] - [NaL^-] - [H_2L]$, $[Na^+] = 2m_2 - [\ NaL^-]$; where, m_2 is the concentration of sodium carbonate. Then, the ionic strength takes its first approximated

Table 5. *K* values of for tartrate buffer at different solvent compositions and different temperatures.

K	***tert*-Butanol (%)**	**Temperature (°C)**				
		30	**35**	**40**	**50**	**60**
$K_1 \times 10^4$	10	6.124	6.442	6.310	6.501	6.180
	20	4.325	4.477	4.446	4.349	4.446
	30	2.761	2.864	2.985	2.985	3.055
	40	1.849	1.795	1.901	1.897	2.193
	50	1.089	1.312	1.312	2.009	1.656
$K_2 \times 10^5$	10	3.119	2.793	2.754	2.685	2.767
	20	2.143	1.892	1.746	2.005	1.730
	30	1.358	1.245	1.362	1.279	1.097
	40	0.869	0.966	0.971	0.811	0.867
	50	4.457	1.489	1.972	1.496	0.499
$\mathrm{K_D} \times 10^4$	10	0.246	0.252	0.218	0.224	0.186
	20	0.136	0.139	0.134	0.085	0.110
	30	1.865	4.083	4.898	2.404	0.977
	40	2.593	1.613	1.043	0.978	1.017
	50	0.444	0.093	0.040	0.016	0.046

Table 6. Calculated average values of rate constants ($k_{ip} \times 10^5$ in sec^{-1}) for the aquation of $[Co(NH_3)_5Br]^{2+}$ in tartrate buffer containing *tert*-butanol (10-50%) at different temperatures.

Temperature (°C)	***tert*-Butanol %**				
	10	**20**	**30**	**40**	**50**
30	0.74	0.38	0.35	1.52	0.61
35	1.51	1.03	1.03	1.88	1.70
40	2.94	2.82	2.96	4.35	5.27
50	11.20	12.60	8.56	17.30	17.40
60	28.00	27.70	24.30	-	49.80

Table 7. Calculated average values of rate constants ($k_{ip} \times 10^5$ in sec^{-1}) for the aquation of $[Co(NH_3)_5Cl]^{2+}$ in tartrate buffer containing *tert*-butanol (10-50%) at different temperatures..

Temperature (°C)	***tert*-Butanol %**				
	10	**20**	**30**	**40**	**50**
30	0.12	0.17	0.30	0.27	0.19
35	0.30	0.30	0.42	0.46	0.47
40	0.51	0.67	0.93	0.79	0.76
50	2.03	2.40	2.30	2.62	2.76
60	7.02	5.42	4.95	-	6.26

value and then γ_1 and γ_2 after which the following terms take their new value

$$[H^+] = K_2 [HL^-] / [L^{2-}] \gamma_2 \tag{14}$$

$$[H_2L] = [HL^-][H^+] \gamma_1^2 / K_1 \tag{15}$$

$$[HL^-] = 2m_1 - 2m_2 - 2[H_2L] - [H^+] \tag{16}$$

$$[L^{2-}] = m_1 - [HL^-] - [H_2L] - [CpXL] - [NaL^-] \tag{17}$$

$$[NaL^-] = [Na^+] [L^{2-}] \gamma_2 / \mathrm{K_{NaL^-}} \tag{18}$$

$$[CpXL] = m_3/[(K_D/ \gamma_2^2 [L^{2-}]) +1] \tag{19}$$

$$[CpX^{2+}] = m_3 - [CpXL] \tag{20}$$

The values of K_1, K_2 and K_D are listed in Table 5 [20]. 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 [CpXL] becomes equal to or less than 1×10^{-7}. The calculated average values of k_{ip} in tartrate media with different percentage of *tert*-butanol at different temperatures are collected in Tables 6 and 7.

3.1. Variation of the rate constant with changing the leaving group

The Co(III) complexes were chosen in this work in order to show the influence of the change of the leaving group (Cl^- and Br^-) of the complex ion on the different kinetic parameters. The values of the rate constant k_0 at the same conditions of the aquation of $[Co(NH_3)_5Br]^{2+}$ are greater than that aquation of $[Co(NH_3)_5Cl]^{2+}$ as shown in Tables 1-4.

These results are attributed to the greater size of the bromide ion. However, the increasing field strength in a spectrochemical series is increasing through the series $I^- < Br^- < Cl^-$ [21]. But the leaving group characteristics will not affect the values of dissociation constant $\mathrm{K_D}$ for both complexes at the same condition. This result was confirmed by Amira *et al.* [22]. They concluded that the dissociation constant $\mathrm{K_D}$ of the series $[Co(NH_3)_5X]^{2+}...L^{2-}$ to be the same for $X^- = Cl^-, Br^-, I^-$ since the cations are all of similar size and structural characteristics.

3.2. Variation of ion-pair coefficients (k_{ip}) with solvent parameter (Dielectric constant)

Tert-butanol is a dipolar protic solvent [23], 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. Furthermore, it was found that *tert*-butanol has a greater effect on the solvent structure than other solvent used earlier. This is 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 For that reason, log k_{ip} was plotted against reciprocal of the dielectric constant D^{-1}, for both $[Co(NH_3)_5Br]^{2+}$ and $[Co(NH_3)_5Cl]^{2+}$ complexes at 30 °C. The dielectric constant values of different compositions are obtained from Akerlof data [24]. As shown in Figures 2 and 3, the plots were found to be non-linear in accordance with the general observations found in the aquation of a large number of other cobalt(III) complexes [25,26] in water-cosolvent mixtures, which led to a

Table 8. Values of multiparameters at different percentage by volume of *tert*-butanol [28].

***tert*-Butanol (*v*:*v*, %)**	**α**	**β**	**π***
10	1.13	0.25	1.03
20	1.09	0.31	0.99
30	1.05	0.39	0.91
40	1.11	0.46	0.86
50	0.90	0.63	0.72

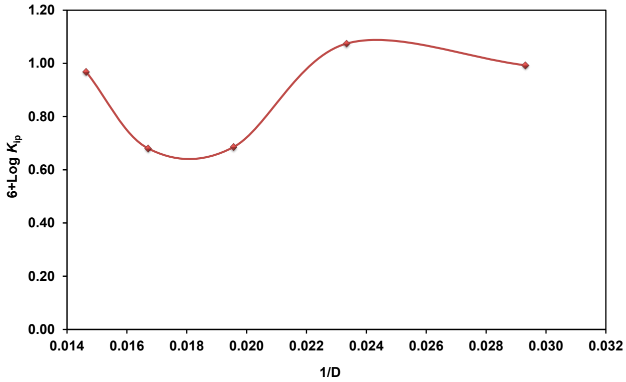

Figure 2. Log k_{ip} *vs* 1/D of tartrate buffer at different % by volume of *tert*-butanol for $[Co(NH_3)_5Brl]^{2+}$ at 30 °C.

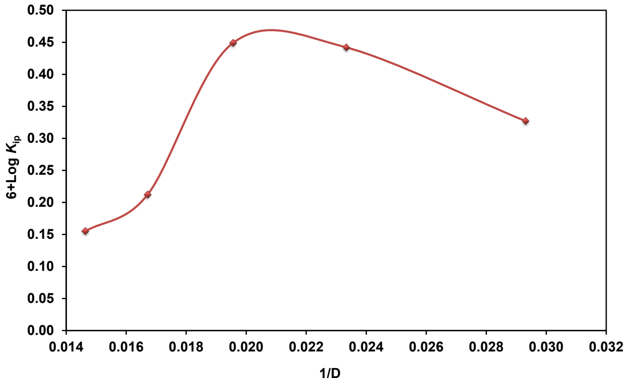

Figure 3. Log k_{ip} *vs* 1/D of tartrate buffer at different % by volume of *tert*-butanol for $[Co(NH_3)_5Cl]^{2+}$ at 30 °C.

conclusion, that the contribution of the non-electrostatic part of solvent effect, overcomes the electrostatic component part. Also, this parameter measures macroscopic property, while specific solute-solvent interactions occur on a microscopic scale is 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 [27].

In order, to obtain a deeper insight into the specific co-solvent interactions which influence reactivity, an attempt was made to adopt the solvatochromic composition method developed by Kamlet *et al.* [28]. This powerful method may be used to quantify, correlate and rationalize multi-interacting solvent effects on reactivity. Thus, the rate data were correlated with the solvatochromic parameters in the form of the following linear solvation energy relationship (LSER) Equation (21).

$$\text{Log } k = A_0 + s.\pi^* + a.\alpha + b.\beta \quad (21)$$

where π* is an index of dipolarity/polarizibility, which measures the ability of the solvent to stabilize a charge or a dipole, α is the HBD (hydrogen bond donor) acidity, β is the HBA (hydrogen bond acceptor) basicity of the solvent in a solute-to-solvent hydrogen bond and A_0 is the regression value of the solute property, the regression parameters s, a and b are solvatochromic coefficients. The values of multiparameters of *tert*-butanol at different percentage by volume are shown in Table 8.

From the values of multiparameters shown in Table 8, we can conclude that upon increasing the percentage of *tert*-butanol, α and π* decreases while β increases. If it was supposed that *tert*-butanol could be considered as a methanol derivative in which a hydrogen atom is replaced by electron-donating groups, thus its hydrogen bond donor ability decreases while the hydrogen bond acceptor ability increases.

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 Tables 9 and 10 at different composition of *tert*-butanol for both complexes. 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*-$[Copy_4Cl_2]^{1+}$ [29] and $[Co(NH_3)_5Br]^{2+}$ [30] where the structure formation becomes greater at lower values of x_2.

Table 9. Values of the thermodynamic parameters of the ion-pairing aquation of $[Co(NH_3)_5Br]^{2+}$in tartrate buffer at different mole fraction *tert*-butanol at 40 °C.

x_2 (Mole fraction)	ΔH^*_{ip} (kJ/mole)	ΔS^*_{ip} (J/K.mole)	ΔG^*_{ip} (kJ/mole)
0.020	95.09	-27.55	103.71
0.045	118.03	42.64	104.68
0.075	113.06	26.76	104.67
0.112	100.60	-7.30	102.89
0.116	111.92	28.46	103.00

Table 10. Values of the thermodynamic parameters of the ion-pairing aquation of $[Co(NH_3)_5Cl]^{2+}$in tartrate buffer at different mole fraction *tert*-butanol at 40 °C.

x_2 (Mole fraction)	ΔH^*_{ip} (kJ/mole)	ΔS^*_{ip} (J/K.mole)	ΔG^*_{ip} (kJ/mole)
0.020	104.34	-12.59	108.28
0.045	98.96	-29.25	108.11
0.075	72.48	-112.11	107.57
0.112	82.97	-77.64	107.27
0.116	94.98	-41.18	107.56

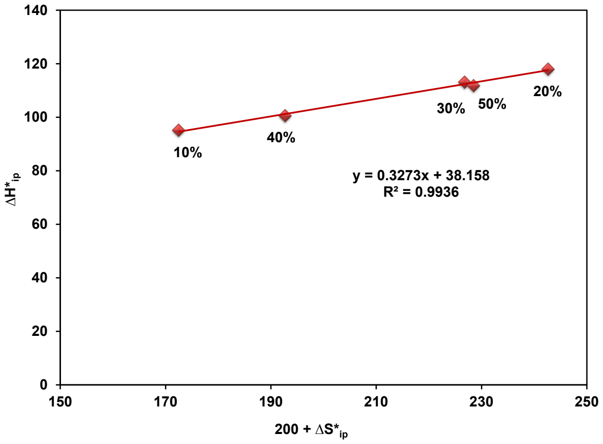

Figure 4. ΔH^*_{ip} *vs* ΔS^*_{ip} for the same buffer at different solvent compositions for $[Co(NH_3)_5Br]^{2+}$ at 40 °C.

At the lower x_2, 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 *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 Tables 9 and 10 by which linear plots are observed between ΔG^*_{ip} against x_2 indicating the presence of compensation effect between ΔH^*_{ip} and ΔS^*_{ip}.

3.4. Isokinetic relationship

The differences in (ΔG^*_{ip}, ΔH^*_{ip} and ΔS^*_{ip}) quantities from one reaction to another in series of reactions that obey a linear free energy relationship are given by Equation (22):

$$\partial \Delta G_{ip}{}^* = \partial \Delta H_{ip}{}^* - \partial T \Delta S_{ip}{}^* \tag{22}$$

When $\partial \Delta S_{ip}{}^* = 0$ such series is said to be isoentropic and in such case $\partial \Delta G_{ip}{}^* = \partial \Delta H_{ip}{}^*$ on the other hand, when $\partial \Delta H_{ip}{}^* = 0$, such series is said to be isoenthalpic. Leffler *et al.* [31] had proposed the more general relationship as shown in Equation (23) that the differences in entropy changes are proportional to the difference in enthalpy changes.

$$\partial \Delta H^*_{ip} = \beta \partial \Delta S^*_{ip} \tag{23}$$

Substituting in Equation (22):

$$\partial \Delta G^*_{ip} = \partial \Delta H^*_{ip}\left(1 - \frac{T}{\beta}\right) \tag{24}$$

$$\partial \Delta G^*_{ip} = \partial \Delta S^*_{ip}(\beta - T) \tag{25}$$

The isoenthalpic and the isoentorpic series are special cases of Equations (24) and (25), where β is infinite and zero, respectively. It could be concluded that at temperature below β, the reaction rate is controlled by $\partial \Delta H_{ip}{}^*$ (i.eenthalpic controlled). At temperature above β, however the controlling factor is $\partial \Delta S_{ip}{}^*$ (i.e entropic controlled). When T = β, equations (24 and 25) inform us that $\partial \Delta G_{ip}{}^* = 0$, i.e all reactions in the set will proceed at the same rate. βis thus known as the isokinetic temperature and can be determined experimentally as the slope of the ΔH^*_{ip} versus ΔS^*_{ip} of the linear plots as shown in Figures 4 and 5).

The computed values of the isokinetic temperatures are found to be more or less constant (1000 × slope). The average values of temperatures for different compositions of solvent with respect to tartrate acid are 327 K for $[Co(NH_3)_5Br]^{2+}$ and 321 K for $[Co(NH_3)_5Cl]^{2+}$.

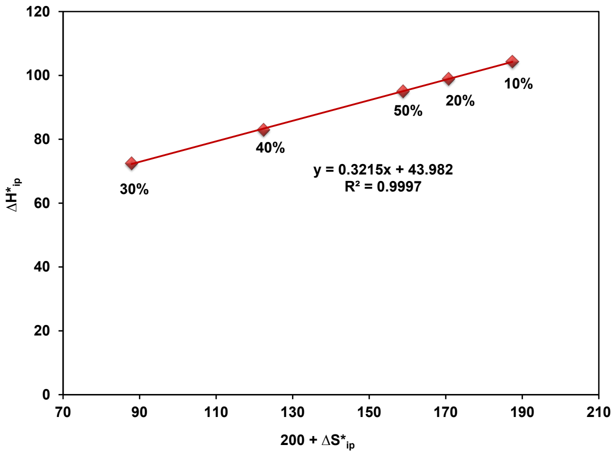

Figure 5. $\Delta H^{*}_{\mathrm{ip}}$ *vs* $\Delta S^{*}_{\mathrm{ip}}$ for the same buffer at different solvent compositions $[Co(NH_3)_5Cl]^{2+}$ at 40 °C.

This means that the compensation effect exists. 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. Application of more exact theories to these effects leads to the result that they will generally give rise to a fairly exact compensation between $\Delta H^{*}_{\mathrm{ip}}$ and $T\Delta S^{*}_{\mathrm{ip}}$, and therefore to a very small effect on $\Delta G^{*}_{\mathrm{ip}}$ which is the case of the presented work.

4. Conclusion

The observed rate constant of $[Co(NH_3)_5Br](ClO_4)_2$ was noted to be greater than $[Co(NH_3)_5Cl](ClO_4)_2$, this is due to the increasing field strength of ligand in a spectrochemical series. 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 and confirms the differential effect of solvent structures between the initial and the transition states. Moreover, an attempt was made to adopt the solvatochromic composition method developed by Kamlett and Taft. The free energy of activation $\Delta G^{*}_{\mathrm{ip}}$ ismore or less linearly varied with the mole fraction of *tert*-butanol indicating of the presence of compensation effect between $\Delta H^{*}_{\mathrm{ip}}$ and $\Delta S^{*}_{\mathrm{ip}}$. Thus the diagrams of $\Delta H^{*}_{\mathrm{ip}}$ and $\Delta S^{*}_{\mathrm{ip}}$ 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 led to only small changes in $\Delta G^{*}_{\mathrm{ip}}$.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

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References

[1]. Glavas, M.; Reynolds, W. L. *J. Chem. Soc. A* **1976**, 1954-1959.
[2]. Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80(11)*, 2642-2646.
[3]. Langford, C. H. *Inorg. Chem.* **1964**, *3*, 228-231.
[4]. Adamson, A. W.; Basolo F. *Acta Chem. Scand.* **1955**, *9*, 1261-1274.
[5]. Moore, W.; Pearson, R. G. *Inorg. Chem.* **1964**, *3*, 1334-1336.
[6]. Ismail, A. M.; Seleim, S. M.; Zaghloul, A. A.; Amira, M. F. *Eur. J. Chem.* **2012**, *3(2)*, 196-201.
[7]. Zeitouni, F. S.; Chaaban, J. K.; Hamed, R. K. *Eur. J. Chem.* **2017**, *8(3)*, 273-278.
[8]. Jones, T. P.; Phillips, J. K. *J. Chem. Soc.* **1968**, 674-679.
[9]. Amira, M. F.; Abdel-Halim, F. M.; El-Semongy, M. M. *J. Electro. Chem. Soc. India* **1982**, *31*, 597-605.
[10]. El-Naggar, G. A.; Seleim, S. M.; Zaghloul, A. A.; Amira, M. F. *Z. Phys. Chem.* **2002**, *216*, 1239-1260.
[11]. Zeitouni, F. S.; El-Subruiti, G. M.; Younes, G. O.; Amira, M. F; *Eur. J. Chem.* **2011**, *2(4)*, 489-494.
[12]. Zeitouni, F. S; El-Subruiti, G. M.; Younes, G. O.; Amira, M. F. *Adv. Mat. Res.* **2011**, *324*, 166-169.
[13]. Hunt, H. R.; Taube, H. *J. Am. Chem. Soc.* **1958**, *80*, 2642-2646.
[14]. Loeliger, D. A.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1376-1380.
[15]. Baldwin, M. E.; Chan, S. C.; Tobe, M. L. *J. Chem. Soc.* **1961**, 4637-4645.
[16]. Searle, G. H.; Sargesson, A. M. *Inorg. Chem.* **1967**, *6*, 2172-2180.
[17]. Hynes, A.; Yanowski, L. K.; Shiller, M. *J. Am. Chem. Soc.* **1938**, *60*, 3053-3054.
[18]. Atkins P.; Paula, J. Physical Chemistry, 8th edition, W. H. Freeman and Company, USA, 2006.
[19]. Wyatt, P. A. H.; Davies, C. W. *Trans. Faraday Soc.* **1949**, *45*, 774-780.
[20]. Hamdan, K.; "Thermodynamic Behavior of some Ion-Pairs in Mixed Solvents", Beirut Arab University Library, 2002.
[21]. Jorgensen, C. K.; Absorption Spectra and Chemical Bonding in Complexes, Pergamon, Elmsford, New York, 1962.
[22]. Amira, M. F.; Carpenter, P.; Monk, C. B. *J. Chem. Soc. , Dalton Trans.* **1980**, 1726-1730.
[23]. Reichardt, C.; Solvent and Solvent Effects in Organic Chemistry, 3rd edition, VCH, Federal Republic of Germany, 2003.

[24]. Akerlof, G. *J. Am. Chem. Soc.* **1932**, *54*, 4125-4139.
[25]. El-Subruiti, G. M.; Younes, G. O.; Zeitouni, F. S.; Amira, M. F. *Int. J. Chem. Kinet.* **2004**, *36*, 494-499.
[26]. El-Subruiti, G. M.; Younes, G. O.; Zeitouni, F. S.; Amira, M. F. *Int. J. Chem. Kinet.* **2008**, *40*, 416-422.
[27]. Laidler, K. J.; Landskroener, P. A. *Trans. Faraday Soc.* **1956**, *52*, 200-210.
[28]. Kamlet, M. J.; Abboud, J. M.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877-2887.
[29]. Elgy, C. N.; Wells, C. F. *J. Chem. Soc. Faraday Trans.* **1983**, *79*, 2367-2376.
[30]. Eid, A. E.; Wells, C. F. *J. Chem. Soc. Faraday Trans.* **1981**, *1*, *77*, 1621-1628.
[31]. Leffler, J. E; Grunwald, E., Rates and Equilibria of Organic Reactions, John Wiley and Sons, New York, 1963.