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Kinetics and mechanism of aquation of bromopentammine cobalt(III) cation assisted by ion-pairing succinate anion in ethane-2-diol-water mixtures

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ABSTRACT

The aquation kinetics of bromopentammine cobalt(III) ion has been investigated in the presence of different concentrations of succinate ion in aqueous medium and that mixed with ethane-1,2-diol (up to 50%, w/w) within the temperature range (35-65 ^oC). The ion-pairing succinate ion concentration (L) and the observed rate constant have been determined at different experimental conditions. The thermodynamic parameters of activation have been calculated and discussed in terms of solvent effects. Also the extrathermodynamic analyses of the obtained results have been discussed on the basis of solute-solvent and solvent-solvent interactions. An empirical correlation between the rate coefficient and the concentration of the ion-pairing succinate ligand (L) has been established and a suggested reaction mechanism is proposed.

1. Introduction

Despite the observation that ion-association is kinetically significant in solution, there are relatively few studies on the kinetic nature of these ion-paired entities in mixed solvent media.

Jones *et al.* [1] found that the correlation of the rate coefficient, k_{obs} with the stiochiometric concentration of the univalent ligand is linear for the aquation of $[Cr(NH_3)_5Cl]^{+2}$ while that of the divalent dicarboxylate ligands is non linear.

Amira *et al.* [2-8] have described the ion-pairing effects on the rate of aquation of chloro, bromopentamminecobalt(III) perchlorate and chloropentamminechromium(III) perchlorate in only one percent (10 or 20%) mixed aqueous organic solvent of some dicarboxylate solutions.

The present work is focused on the kinetic solvent effects of the aquation of bromopentamminecobalt(III) ion, in the presence of ion-pairing succinate anion in aqueous medium and in binary mixtures of water and ethane-1,2-diol (up to 50%) at different temperatures. This sort of study will assist for highlighting any new correlations based on thermodynamic and extra thermodynamic analysis of the obtained kinetic data. Besides the Linear Free Energy Relationship (and other similar relations) has been examined to show the role of solvent on the ion-pair aquation reaction. Succinate solutions are of special interest due to their reactivity spectrum toward ion-pairing and ion solvation effects which leads to important theoretical and practical importance.

2. Experimental

Succinic acid (B.D.H. Analar) was recrystallized. Ethane-1,2-diol (B.D.H. Analar) was redistilled, and mixtures were prepared using double distilled water. The $[Co(NH_3)_5Br]\ Br_2$ complex was prepared by the method of Booth [9] and then converted to the nitrate salt and recrystallised form. Na_2CO_3 (B.D.H.) was dried at 300 ^oC for 3 hr.

2.1. Equipments and kinetic measurements

Spot Galvanometer with an internal resistance of 60 Ohms and sensitivity of $2x10^{-8}$ A. per mm. scale division was connected in series with the chemical cell, $Ag/AgBr_{(s)}/Br^-/KNO_3$/Buffer, H_2Q, Q, Pt. For the purpose of determining the liberated bromide ion from the aquation reaction potentiometerically [8]. This method of analysis is preferred due to its high reproducibility and the good agreement of its rate constant values with those obtained spectrophotometrically [2].

3. Results and discussion

A series of kinetic runs for the aquation of bromopenta amminecobalt(III) ion were performed in succinate buffer (80% neutralization of succinic acid (m_1) by Na_2CO_3 (m_2) containing different percentages of ethane-1,2-diol (up to 50%, w/w) within the temperature range (35-65 ^oC). A linear least square method was used to fit the obtained first order kinetic data according to the kinetic Equation 1,

$$Ln\frac{V_\infty}{V_\infty - V_t} = k_{obs}\, t \qquad (1)$$

where V_t is the potentiometric titration reading at time (t) and V_∞ is the infinity titre which was calculated from the known initial concentration of the complex salt (m_3). For each temperature and solvent composition, a set of kinetic runs

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were conducted for different stoichiometric concentrations of the dicarboxylate ligand. The obtained least square rate constant k_{obs}, at different experimental conditions are listed in Table 1.

Garrick [10] found that the rate of aquation of chloropenta amminecobalt(III) ion was slightly increased by chloride, nitrate, chlorate, formate and acetate anions while sulphate cause marked acceleration. Garrick expressed his results in terms of, Equation 2.

$$k_{obs} = k_1 + k_2 C_L \qquad (2)$$

where, k_{obs} is the observed pseudo-unimolecular rate constant, k_1 its value in the absence of L, k_2 is the catalytic coefficient and C_L is the stiochiometric concentration of the univalent ligand. Jones, Harris and Wallace [11] on testing the last equation found that the plots of k_{obs} against C_L of univalent ligands were linear and extrapolated to a common k_1 at $C_L = 0$ while for divalent ligands the plots are nonlinear.

In the present investigation, it is now necessary to examine the possible empirical correlations in the succinate ion solutions containing different concentrations of ethylene glycol (up to 50%) where the added ethylene glycol lowered the dielectric constant which assist the ion-association process. The stoichiometric concentration of the succinate ion can be expressed by the stoichiometric cabroxylic acid concentration (m_1). Firstly most plots of k_{obs} versus m_1 for different succinate ion at different solvent compositions gave nonlinear plots radiating from k_1 (rate constant in absence of succinate ion). This nonlinear correlation is agreed with the work of Jones, Harris and Wallace [11] for divalent ion-pairing ligands (like dicarboxylates). These plots are refined by using the free succinate ion concentration [L] instead of $m_1$which is reprehensive in Figure 1.

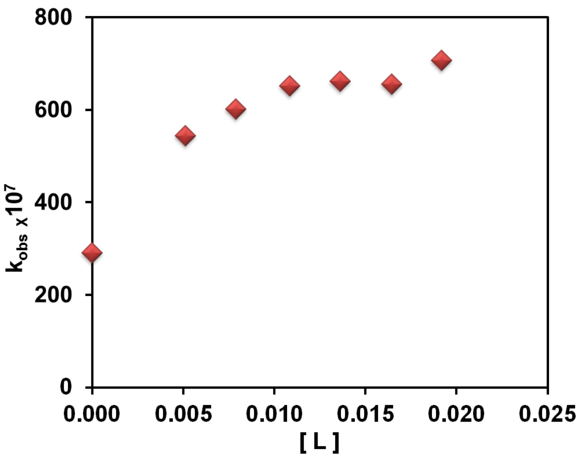

Figure 1. Variation of k_{obs} versus [L] for succinate ion at 45 °C for 50% solvent composition.

Different attempts were tested and one of them was only valid in which the plots of $1/(k_{obs}-k_1)$ versus 1/[L] (L is L^{2-}) give a straight line with a positive slope and positive intercept, as shown in Figure 2. This linearity leads to the following empirical correlation (Equation 3).

$$\frac{1}{(k_{obs}-k_1)} = a + \frac{b}{[L]} \qquad (3)$$

where a and b are empirical constants and their values for different cases are listed in Table 2. Equation 3 can take another form, Equation 4.

$$k_{obs} = \frac{k_1 + \left[k_1(a/b) + 1/b\right][L]}{1 + (a/b)[L]} \qquad (4)$$

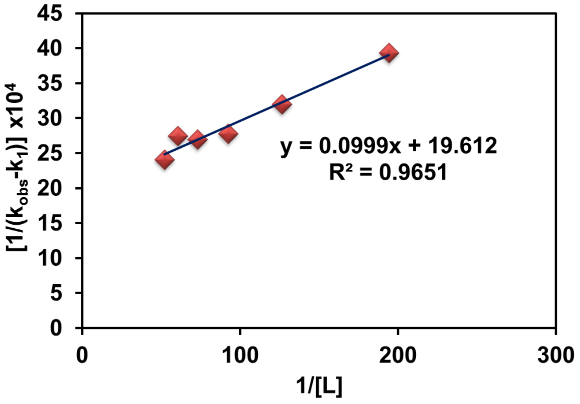

Figure 2. Plot of 1 / (k_{obs} – k_1) versus [L] for succinate ion at 45 °C for 50% solvent composition.

Data in Table 2, shows that values of the empirical constants a and b depend on the solvent composition which arises from the solute-solvent and the solvent-solvent interactions.

In presence of succinte ions, an ion-pair is formed and the aquation reaction can be represented as:

$$\mathrm{CpX^{2+} + H_2O \overset{k_1}{\rightleftharpoons} [CpXH_2O]^{2+}} \qquad (5)$$

$$\mathrm{CpXL + H_2O \overset{k_{ip}}{\rightleftharpoons} [CpXH_2O]^{2+} + L^{+}} \qquad (6)$$

where, $CpXL$ is the ion-pair concentration, CpX^{+2} is the free complex ion concentration and k_{obs} is related to k_{ip} according to Wyatt and Davies treatment [12].

The principle of calculations of ion-pair rate constant k_{ip}, were discussed before [2]. K_1, K_2 and K_D values taken from references [13,14].The calculation of the free ion-pairing succinate concentration [L] is based on the following set of equations, and Table 3 collects the average k_{ip} values at different conditions.

$\mathrm{CpXL \leftrightarrows CpX^{2+} + L^{2-}}$ K_D (7)

$\mathrm{NaL^- \leftrightarrows Na^+ + L^{2-}}$ K_{NaL^-} (8)

$\mathrm{H_2L \leftrightarrows HL^- + H^+}$ K_1 (9)

$\mathrm{HL^- \leftrightarrows L^{2-} + H^+}$ K_2 (10)

$K_D = [CpX^{2+}][L^{2-}]\, f^2_2 / [CpXL]$ (11)

$K_1 = [H^+][HL^-]\, f_1^2 / [H_2L]$ (12)

$K_2 = [H^+][L^{2-}]\, f_2 / [HL^-]$ (13)

$K_{NaL^{-}} = [Na^+][L^{2-}]\, f_2 / [NaL^-]$ (14)

where f_1 and f_2 are the activity coefficients of the univalent and divalent ions respectively. Their values were obtained from Debye-Huckel equation in the form $\log f = -A\,(I^{½}/1+I.3I^{½})-0.3I$ where I is the ionic strength,

Table 1. Values of rate constant k_{obs}, for the aquation of $[Co(NH_3)_5\,Br]^{2+}$ in succinate media at different composition of ethylene glycol.

%	35 °C		45 °C		55 °C		65 °C	
	10^3 [L]	k_{obs}* x10^7	10^3 [L]	k_{obs}* x10^7	10^3 [L]	k_{obs}* x10^7	10^3 [L]	k_{obs}* x10^7
0	5.39	236.5	5.26	679.8	4.78	2463.9	5.28	9113.7
	8.09	245.8	8.19	774.1	7.31	2489.2	7.97	7081.7
	10.84	250.0	10.72	784.4	9.73	2527.9	10.76	9063.9
	13.57	255.0	13.48	806.6	12.20	2698.4	13.47	11845.8
	16.20	257.3	16.14	848.4	14.64	2629.8	16.11	11602.4
	18.81	263.1	18.66	885.1	17.09	2925.4	18.76	12195.5
10	5.34	246.2	5.33	702.7	5.26	2329.2	5.31	10713.5
	8.10	259.4	8.07	762.8	8.02	2567.6	8.056	10293.1
	10.79	268.1	10.77	733.8	10.76	2647.4	10.83	9583.9
	13.53	275.5	13.46	813.3	13.48	2656.7	13.56	11534.6
	16.21	280.8	16.06	793.5	16.07	2728.6	16.17	11327.6
	18.77	285.1	18.77	839.9	18.66	2816.0	18.95	11412.2
20	5.34	178.0	5.19	475.0	5.25	2551.2	5.23	8267.4
	8.13	173.5	8.05	500.7	8.05	2909.7	8.00	10725.0
	10.91	190.0	10.83	526.8	10.80	2848.7	10.79	9498.6
	13.65	194.5	13.48	577.1	13.50	2581.6	13.51	10368.4
	16.27	198.3	16.20	612.2	16.19	2919.6	16.22	13870.6
	18.99	187.4	18.81	650.9	18.82	2402.3	18.87	11777.3
30	5.24	180.4	5.18	625.4	5.17	2382.0	5.16	7660.3
	8.03	188.8	7.94	704.5	7.99	2566.3	7.96	8782.6
	10.84	193.8	10.76	688.8	10.79	2681.2	10.76	8420.1
	13.58	196.8	13.56	742.6	13.55	2780.0	13.52	9623.7
	16.34	202.1	16.31	731.8	16.27	2682.8	16.28	9874.5
	18.98	203.3	18.85	762.6	19.02	2792.1	19.02	9299.4
40	5.17	186.7	5.27	612.5	5.09	2188.7	5.04	8008.4
	7.99	220.0	8.05	622.6	7.90	2426.3	7.78	9165.7
	10.81	196.1	10.84	667.8	10.72	2407.6	10.65	9698.0
	13.62	199.8	13.67	696.7	13.36	2382.2	13.43	7498.0
	16.34	215.0	16.39	720.4	16.13	2351.3	16.17	10538.5
	19.07	204.6	19.08	698.2	18.91	2468.0	18.98	8680.1
50	5.14	211.0	5.15	544.3	4.94	2095.3	5.00	6831.5
	7.97	539.6	7.90	602.5	7.74	1651.3	7.79	7963.1
	10.80	692.8	10.81	650.5	10.67	2416.9	10.71	7810.8
	13.65	285.0	13.63	661.1	13.38	2464.0	13.44	7600.1
	16.39	438.0	16.43	654.2	16.24	2559.6	16.31	8064.5
	19.15	356.0	19.15	705.7	18.97	2661.8	19.09	8476.9

Table 2. Values of (a, b and a/b) (a = Intercept, b = Slope) of equation 1 for succinate ion at different composition of ethylene glycol.

W/W, %[a]	Succinate ion		
	a	b	a/b
0	-8.7453	0.7465	-11.715
10	23.1520	0.1045	221.550
20	8.7441	0.6695	13.061
30	19.8020	0.0699	283.290
40	21.8470	0.0661	330.514
50	19.6120	0.0999	196.316

[a] w/w, % of ethan-1,2 diol.

Table 3. Average values of ion-pair rate constant $10^5\,k_{ip}$ (s^{-1}) at different experimental conditions for succinate ion.

W/W, %[a]	Temp. °C			
	35	45	55	65
0	3.4	10.9	34.8	179.7
10	4.2	12.7	38.7	180.9
20	2.6	8.4	44.6	146.6
30	2.7	11.3	39.4	131.4
40	2.9	10.2	33.4	116.3
50	4.6	9.3	35.3	110.3

[a] w/w, % of ethan-1,2 diol.

$$I = 0.5\,([H^+] + [HL^-] + 4\,[L^{2-}] + 4\,[CpX^{2+}] + 2m_3 + [Na^+] + [NaL^-]) \qquad (15)$$

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

$$m_3 = [CpX^{2+}] + [CpXL] \qquad (17)$$

where m_3 is the stoichiometric concentration of the complex ion, ($m_3 = [CpX^{2+}] + [CpXL]$), k_1 is the observed rate constant in the absence of the succinate ion-pairing ligand (X = Br).

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

For the first cycle

$$[H^+] = 0,\ [CpXL] = 0,\ [NaL^-] = 0 \qquad (18)$$

$$[CpX^{2+}] = m_3 - [CpXL],\ [HL^-] = 0.5\ m_2\ [H_2L] = 0.3\ m_1 \qquad (19)$$

$$[L^{2-}] = m_1 - [HL^-] - [CpXL] - [NaL^-] - [H_2L] \qquad (20)$$

$$[Na^+] = 2\ m_2 - [NaL^-] \qquad (21)$$

Then the ionic strength takes its first approximated value and then f_1 and f_2 ($f_2 = 4\ f_1$) after which the following terms take their new values as,

$$[H^+] = K_2\,[HL^-] / [L^{2-}]\ f_2 \qquad (22)$$

$$[H_2L] = [HL^-]\,[H^+]\ f^{\,2}{}_1 / K_1 \qquad (23)$$

$$[HL^-] = 2\ m_1 - 2m_2 - 2[H_2L] - [H^+] \qquad (24)$$

$$[L^{2-}] = m_1 - [HL^-] - [H_2L] - [CpXL] - [NaL^-] \tag{25}$$

$$[NaL^-] = [Na^+][L^{2-}]\, f_2 / K_{NaL^-} \tag{26}$$

$$[CpXL] = m_3 / [(K_D / f_2^2\, [L^{2-}]) + 1] \tag{27}$$

$$[CpX^{2+}] = m_3 - [CpXL] \tag{28}$$

and then I, f_1 and f_2 recalculated again. These steps of calculations were repeated many times until the difference between two successive values of [L] becomes equal to (or less than) 10^{-7}.

3.1. Variation of activation parameters with solvent composition

The thermodynamic parameters of the ion-pairing aquation reactions, ΔG^*_{ip}, ΔH^*_{ip} and ΔS^*_{ip} were calculated at 25 °C using least square procedure program, and these values with their standard deviations are given in Table 4. ΔG^*_{ip} values show a small increase with increase the mole fraction of the co-solvent, giving a good indication of the compensation between ΔH^*_{ip} and ΔS^*_{ip} .Variation of ΔH^*_{ip} and ΔS^*_{ip} versus the mole fraction of the co-solvent (χ_2) displayed minimum at $\chi_2 = 0.03$ and maximum at $\chi_2 = 0.07$ as shown in Figure 3. These values are found to be close to those obtained of other cobalt complexes in the same solvent system. In dilute aqueous solution ($\chi_2 < 0.1$) ethan-1,2 diol can exist as the gauche cyclic conformer with strong intermolecular hydrogen bonding, which enhances the hydrophobicity of the co-solvent [15]. The enhancement of the solvent structure and structure breaking, as reflected by the maxima and minima in these plots, strongly suggest that the effect of structure perturbations in the bulk phase are effectively transmitted to the reaction zone through the solvent shell of the reactant.

Table 4. Values of the thermodynamic parameters ΔH^*_{ip}, ΔS^*_{ip}, $\Delta G^*_{ip}$of different solvent compositions at 25 °C.

W/W, %^{a}	**ΔH^*_{ip} (Kj/mol)**	**ΔS^*_{ip} (J/K.mol)**	**ΔG^*_{ip}(kJ/mol)**
0	110.38±9.21	26.38±18.57	102.51±17.73
10	104.78±8.45	10.03±16.21	101.79±16.26
20	116.38±6.55	44.02±20.31	103.26±12.61
30	108.56±1.22	20.04±3.78	102.59±2.35
40	103.69±2.06	6.40±4.22	102.43±3.97
50	91.35±9.31	-33.22±18.87	101.23±17.92

^{a} W/W % of ethan-1,2 diol.

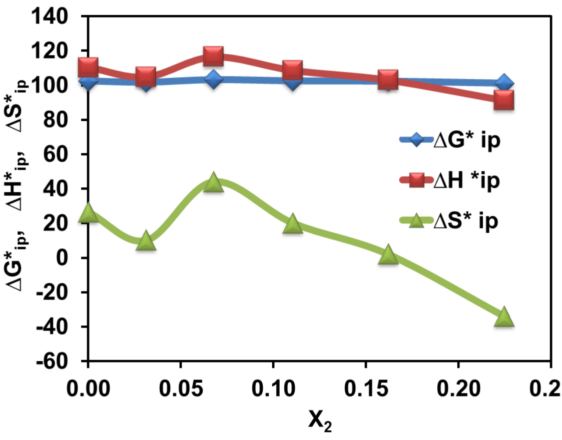

Figure 3. Plot of (ΔG^*_{ip}, ΔH^*_{ip}, ΔS^*_{ip}) versus X_2.

3.2. Extrathermodynamic analysis

In the present work the plot of ΔH^*_{ip} versus ΔS^*_{ip} for the ion-pair aquation reactions at different compositions is linear as shown in Figure 4. The parallel changes in ΔH^*_{ip} and ΔS^*_{ip} lead to only small changes in ΔG^*_{ip} and for such a closely related series, a common reaction mechanism is supported. The obtained isokinetic temperature (β) is 322.4 K.

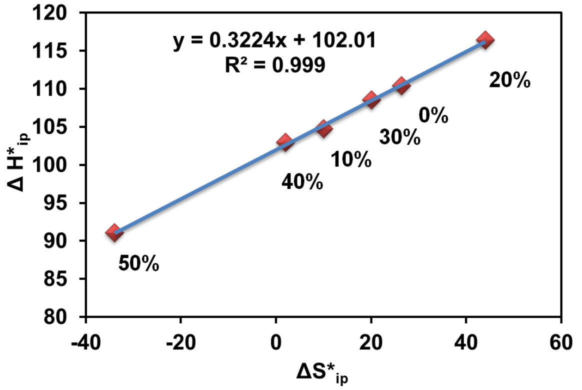

Figure 4. Isokinetic plot of the aquation of $[Co(NH_3)_5Br]^{2+}$ at different solvent composition.

The genuine nature of the isokinetic relationship was verified by the Exner criterion [16] by plotting log $k_{(328\ K)}$ versus log $k_{(318\ K)}$. The value of β was calculated from Equation 29, where *b* is the slope of Exner plot, and the ratio T_1/ T_2 must be smaller than unity.

$$\beta = \frac{T_1 T_2 (b-1)}{b T_2 - T_1} \tag{29}$$

The calculated value of β is 330 K, which lie within the studied temperature range. This means that the compensation effect must be born in mind. The true explanation of compensation effect lie in terms of solvent-solute interactions. Any effect that, 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 generally give rise to a fairly exact compensation between ΔH^*_{ip} and $T\Delta S^*_{ip}$ and therefore to a very small effect on ΔG^*_{ip}.

Although the effect of solvent on the rate and the position of chemical equilibrium has been known, there is still no reliable or exact methods for a quantitative description and prediction of such solvent effects. In the present work the correlations ΔG^*_{ip}-ΔG^o_{ass}, ΔH^*_{ip}-ΔH^o_{ass} and ΔS^*_{ip}- ΔS^o_{ass} were found to be linear at different solvent compositions (0-50%w/w) and can be represented by the following Equation 30.

$$y = mx + c \tag{30}$$

in which y represents ΔG^*_{ip}, ΔH^*_{ip} or ΔS^*_{ip} and x represents ΔG^o_{ass}, ΔH^o_{ass} or ΔS^o_{ass} where these correlations can describe a Linear Free Energy , Linear Enthalpy, and Linear Entropy Relationships . The m and c values were found to be 70.44 and 109, -1.23 and 116, -1.04 and 86.1 for the above relations respectively. These linear correlations can refer to a common reaction mechanism existing within the studied mixed solvent compositions.

3.3. Variation of ion-pair rate constant with dielectric constant and water concentration

Elsemongy and Amira [17] 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 be 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 form, Equation 31),

$$log\frac{A}{k} = \frac{E.b}{2.303\,R\log\left(\frac{C}{D}\right)} \quad (31)$$

(Log C = Log a + 293.15 b) (32)

where A is the frequency factor, a and b are Akerlöf᾽s empirical constants [18]. The log A/k versus Eb/log (C/D) gives a good straight line passing through origin with a slope equal to 0.0520, which is in consistent with the theoretical one (0.0522). This finding add, a further support to this equation.

Also log k_{ip} was plotted against reciprocal of the dielectric constant D at different temperatures, where the dielectric constant values of different compositions are obtained from Akerlöf data [18]. As shown in Figure 5, 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 [19-25] 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, this 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 [26].

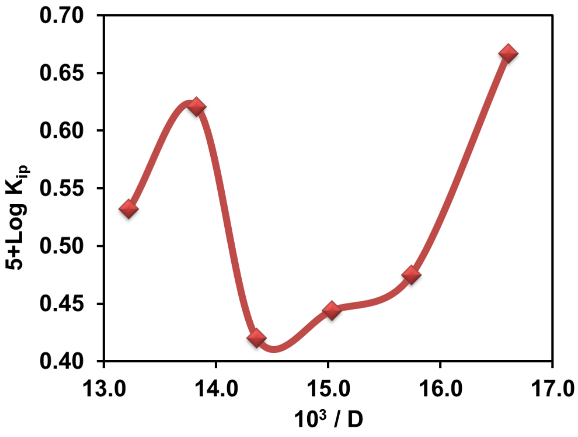

Figure 5. Variation of log k_{ip} versus 1/D at 35 °C.

The plot of the logarithm of ion pair rate constant versus the logarithm of water concentration at constant temperature and varying solvent composition is found to be nonlinear. This nonlinearity can be attributed the complex structure of the mixed solvent medium.

3.4. Proposed reaction mechanism

A proposed reaction mechanism which takes into considerations, the Wyatt and Davies treatment [12], the extrathermodynamic analysis of the obtained kinetic data, the kinetic solvent effects and the empirical correlation of k_{obs} with the free concentration of the ion-pairing succinate ligand is described by the following scheme.

$$CpX^{2+} + L^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CpXL \quad (33)$$

$$CpX^{2+} \xrightarrow{k_2} Cp^{3+} + X \quad (34)$$

$$CpXL \xrightarrow{k_3} CpL^{+} + X \quad (35)$$

Cp^{3+} and CpL^{+} are five coordinate intermediates (kinetic solvent effect)

$$Cp^{3+} + H_2O \xrightarrow{k_4} Cp(H_2O)^{3+} \quad (36)$$

$$CpL^{+} + H_2O \xrightarrow{k_5} Cp(H_2O)^{3+} + L^{2-} \quad (37)$$

where $k_{obs}\,.m_3 = k_4\,[Cp^{3+}] + k_5\,[CpL^{+}]$ (Watt and Davies treatment) and

$$m_3 = [C_p^{3+}] + [C_pL^{+}] \quad (38)$$

i.e. $k_{obs}\,.m_3 = k_4(m_3 - [CpL^{+}]) + k_5\,[CpL^{+}]$ (39)

Therefore

$$k_{obs}\,.m_3 = m_3k_4 + [CpL^{+}]\,(k_5 - k_4) \quad (40)$$

Applying steady state treatment on $[CpL^{+}]$ and $[CpXL]$

$$k_3[CpXL] = k_5\,[CpL^{+}] \quad (41)$$

$$k_1[CpX^{2+}][L^{2-}] = k_{-1}[CpXL] + k_3[CpXL] \quad (42)$$

or

$$k_1(m_3 - [CpXL])\,[L^{2-}] = (k_{-1} + k_3)[\,[CpXL] \quad (43)$$

i.e. $k_1m_3\,[L^{2-}] = \{k_1[L^{2-}] + (k_{-1} + k_3)\}[CpXL]$ (44)

Therefore,

$$[CpXL] = \frac{k_1\,m_3\,[L^{2-}]}{(k_{-1}+k_3)+k_1[L^{2-}]} \quad (45)$$

From Equations 41 and 45

$$[Cp] = \frac{k_3}{k_5}\left\{\frac{k_1m_3(L^{2-})}{(k_{-1}+k_3)+k_1[\,L^{2-}\,]}\right\} \quad (46)$$

Substituting in Equation 40, and rearrangement

Therefore,

$$k_{obs} = \frac{k_4+\left\{\frac{k_1\,k_4}{(k_{-1}+k_3)}+\frac{k_1\,k_3}{k_5}\left(\frac{k_5-k_4}{k_{-1}+k_3}\right)\right\}[L^{2-}]}{1+\frac{k_1}{(k_{-1}+k_3)}[L^{2-}]} \quad (47)$$

Equation 47 discuss the empirical correlation between k_{obs} and $[L^{2-}]$ in which k_1 in Equation 4 is replaced by k_4 in Equation 47, where

$$a/_{b} = \frac{k_1}{k_{-1}+k_3} \quad \text{and} \quad 1/_{b} = \frac{k_1k_3}{k_5}\left\{\frac{k_5-k_4}{k_{-1}+k_3}\right\} \quad (48)$$

and consequently the empirical constant (a) equal to $\frac{k_5}{k_3(k_5-k_4)}$.

4. Conclusion

Our aim in the present investigation was to look for possible correlations between the thermodynamic properties of the activated complex and the corresponding thermodynamic functions of the ion-pair formation reactions within the studied binary composition of the mixtures under investigation. Further we investigated the kinetic solvent effects and the empirical correlation of k_{obs} with the free concentration of the ion-pairing succinate. Third the future work must extended to deal with other solvent systems and other types of dicarboxylate ion-pairing ligands to the throw light on these solvent-solvent and solute-solvent interactions.

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