July, 1988] © 1988 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 61, 2623—2628 (1988) 2623

Kinetics of Substitution of Aqua-Ligands from *cis*-Diaquobis(ethylenediamine)-cobalt(III) Complex by *β*-Alanine and DL-Valine in Various EtOH-Water Mixtures

Debabrata CHATTERJEE and G. S. DE*
Department of Chemistry, University of Burdwan, Burdwan 713104, India

(Received July 30, 1987)

The kinetics of above titled reaction has been studied spectrophotometrically in various water–ethanol mixtures at different temperatures (45—60 °C). The following rate law has been established in the pH range 3.2 to 4.5.

$$\frac{d[\mathrm{Co(en)_2(H_2O)(LH)^{3+}}]}{dt} = \frac{k_a K_E[\mathrm{Co(en)_2(H_2O)_2{}^{3+}}]_T[\mathrm{LH}]}{1 + K_E[\mathrm{LH}]}$$

where LH represents the zwitterionic form of the amino acids viz. *β*-alanine and DL-valine. K_E is the ion-pair equilibrium constant between substrate complex ion and zwitterionic ligand the values of which increase with the increase of organic component of medium, where reverse is true for k_a, the interchange rate constant from outersphere complex to innersphere product. It was observed that at higher ligand concentration a limiting rate is attained, which has been explained due to completion of ion-pair formation. Increasing effect of pH and special catalytic effect of NO_3^- have been observed. Activation parameters (ΔH^{*} and ΔS^{*}) have been calculated and compared with isotopic water exchange reaction and other deaquation reactions. A dissociative interchange mechanism (I_d) involving ion-pair formation has been suggested.

Elucidation of the mechanism of deaquation reactions on Co(III) center in still a lively issue. No single mechanism can be adequate to explain the variety of observations in the water replacement reactions on Co(III) complexes. However, thorough survey[1—7] reveals a general pattern of the mechanism in which replacement of water molecule occurred through either purely dissociative or dissociative interchange pathway. In case of dissociative interchange process, substrate Co(III) complex ion first forms an ion pair with incoming ligand in a very rapid step, then in a slower rate determining step interchange between coordinated water molecule and incoming ligand occurs to give final product. Deviations from the above mechanism are also noticed in which associative (A) and associative interchange (I_a) mechanism have been suggested.[8—10] Therefore the controversy regarding mechanism in water replacement reactions of well studied cobalt(III) aqua–amine (or ammine) system still persists. The variation of substitution rate with solvent composition has also been proved useful for diagnosis of mechanism in octahedral substitution reactions.[11—14] In response to the above fact we have studied the kinetic behavior of *cis*-$[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$ with amino acid ligands viz. glycine,[15] DL-alanine,[16] and L-serine[17] which behaved as good bidentate ligands (NO). The present work is a continuation of our earlier studies having the purpose of assessing the role of solvent composition on water replacement reactions in octahedral Co(III) complex.

Experimental

Substrate complex *cis*-$[\mathrm{Co(en)_2(H_2O)_2}](\mathrm{NO_3})_3$ was prepared by following the literature method[18] and characterized by elemental analysis and spectral data obtained were compared with the data reported in literature.[19] Crystal forms of reaction products were not separated due to their hygroscopic nature. To determine the composition of the reaction product in each case equal volume of solution of substrate complex (0.01 M†) and ligand (*β*-alanine, DL-valine) was mixed separately in three different molar ratios 1:1, 1:2, and 1:3 at fixed pH 4.2. The mixtures were kept at 50 °C for 24 hours. Absorption spectra of all the mixtures were taken and spectral data obtained were compared with the data shown for the product complexes. There is very little difference in absorbances between our product complexes and those cited in literature.[20] Further 1:1 metal–ligand composition of reaction products in solution was verified by Job's method in both cases. There are three possible products expected in solution: (a) $[\mathrm{Co(en)_2L}]^{2+}$, (b) $[\mathrm{Co(en)_2(H_2O)(LH)}]^{3+}$, and (c) $[\mathrm{Co(en)_2(LH)_2}]^{3+}$. Experiment on Job's method of continuous variation, ruled out the possibility of formation of $[\mathrm{Co(en)_2(LH)_2}]^{3+}$. To establish the composition of the product between (a) and (b) we have performed pH metric titration with the reaction product in solution. The result indicates the formation of (b), i.e. $[\mathrm{Co(en)_2(H_2O)(LH)}]^{3+}$. Thus the zwitterionic ligand $^{-}\mathrm{OOC{-}R{-}NH_3}^{+}$ coordinated to metal center through its O- end.

Kinetic Run. The course of the reaction was followed by a HILGER UVISPEK spectrophotometer at 495 nm bacause substantial differences exist in the absorption of substrate complex and it's reaction product (Fig. 1). Equal volume of Complex 1 (substrate complex) and amino acid ligand $[\mathrm{LH}] \gg [\mathrm{Co}]$ was mixed as such that the pseudo-first-order condition is applicable and the pseudo-first-order rate constant values (k_{obs}) were obtained by plotting $\log[(A_\alpha - A_o)/(A_\alpha - A_t)]$ against time, where A_o, A_t, and A_∞ are the absorbance values initially, after time t, and after the

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† $1\ \mathrm{M} = 1\ \mathrm{mol\ dm^{-3}}$.

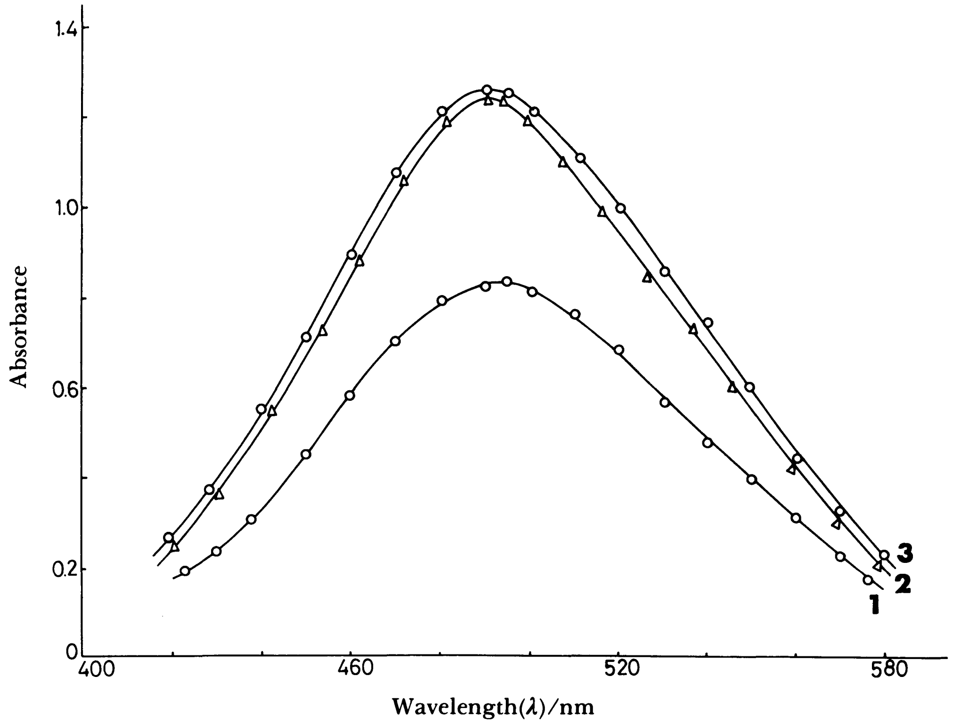

Fig. 1. Spectra of substrate complex *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ (**1**) and it's products $[Co(en)_2(H_2O)(valH)]^{3+}$ (**2**) and $[Co(en)_2(H_2O)(\beta\text{-alaH})]^{3+}$ (**3**).

completion of the reaction respectively. The plot of $\log[(A_\alpha - A_o)/(A_\alpha - A_t)]$ vs. time t gave a good straight line passing through the origin. This linearity is observed from start to finish of the reaction which ruled out the possibility of any consecutive reactions.

Results and Discussion

i) Effect of [Complex 1] on Rate. At fixed ligand concentration [Complex 1] was varied in the range 0.0025 to 0.0075 M keeping pH and ionic strength of the medium fixed at 4.2 and 0.05 M respectively. It is seen that the values of $k_{obs}\times(10^4\ s^{-1})$ are 2.60, 2.61, and 2.64 at [Complex 1]=0.0025, 0.005, and 0.0075 M, where anating ligand is β-alanine. In case of ligand valine pseudo-first order rate constant $k_{obs}\times10^4\ s^{-1}$ values are 1.92, 1.90, and 1.94 at 0.0025, 0.005, and 0.0075 M complex concentrations respectively. These k_{obs} values at different Complex 1 concentrations are in good agreement with the first order rate law with respect to the Complex 1 concentration.

ii) Effect of Varying pH on Rate. When the anating ligand is β-alanine the values of k_{obs} $(\times10^4\ s^{-1})$ are 0.73, 0.95, 1.63, 2.61, and 3.5 at pH 3.2, 3.5, 3.8, 4.2, and 4.5 respectively and for DL-valine k_{obs} $(\times10^4\ s^{-1})$ are 0.87, 1.1, 1.42, 1.90, and 2.30 at the above mentioned pH respectively. Now in the studied pH range 3.2 to 4.5 both the ligand β-alanine and DL-valine exist in zwitterionic forms as β-alaH and DL-valH respectively in solution.[21] Therefore ligands nature is not altered appreciably in the solution. Acid dissociation equilibrium of substrate complex can be represented as follows.

$$cis\text{-}[Co(en)_2(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} cis\text{-}[Co(en)_2(OH)(H_2O)]^{2+} + H^+$$

where the value of pK_1 is 5.8 at 25 °C.[22]

Now considering the above equilibrium effect of pH on observed rate constant can be expressed as follows.

$$k_{obs} = k_1 + k_2K_1[H^+]^{-1} \qquad (1)$$

where k_1 is the observed rate constant when reacting species is diaquo complex and k_2 is the observed rate constant for hydroxoaquo complex. It is seen from Eq. 1 that the increase in pH i.e. decrease in hydrogen ion concentration increases the reaction rate. Plot of k_{obs} vs. $1/[H^+]$ gave a good straight line and deperture from linearity started at higher pH. Actually in the studied pH range 3.2 to 4.5 percentage of diaquo complex in the solution is maximum, however increase in small amount of hydroxaquo complex increases the reaction rate because hydroxoaquo complex is much more reactive (reacts 60 times more faster than diaquo complex)[22] than diaquo species. Again hydroxide ion facilitates the formation of very reactive hydroxo complex which also increases the reaction rate.

iii) Effect of Variation of Ligand Concentration on Rate. The ligand concentration was varied in the range 0.05 to 0.15 M at four different temperatures

Table 1. Values of k_{obs} in Various Ethanol–Water Mixtures at Different Temperatures $[Co(en)_2(H_2O)_2^{3+}]=0.005$ M, pH=4.2, Ionic Strength=0.03 M

Ligand concentration	Temp	$k_{obs}\times10^4/s^{-1}$					
		β-Alanine			DL-Valine		
M	°C	% of ethanol (v/v)			% of ethanol (v/v)		
		10	20	30	10	20	30
0.050	45	0.32	0.37	0.43	0.24	0.27	0.35
	50	0.75	0.84	0.96	0.35	0.41	0.57
	55	1.32	1.61	1.85	1.11	1.32	1.50
	60	2.51	3.05	3.47	2.05	2.32	2.64
0.075	45	0.52	0.59	0.67	0.37	0.41	0.47
	50	1.21	1.30	1.40	0.49	0.62	0.76
	55	2.01	2.34	2.61	1.52	1.72	1.90
	60	3.60	4.20	4.79	3.13	3.40	3.90
0.100	45	0.65	0.70	0.76	0.45	0.52	0.57
	50	1.65	1.78	1.91	0.66	0.85	0.98
	55	2.61	2.98	3.19	1.98	2.25	2.52
	60	4.61	5.60	6.14	3.98	4.25	4.60
0.125	45	0.76	0.85	0.92	0.55	0.59	0.65
	50	1.85	2.00	2.15	0.87	1.00	1.15
	55	3.02	3.40	3.62	2.36	2.71	3.10
	60	6.55	6.80	7.16	4.67	4.97	5.40
0.150	45	0.88	0.95	1.05	0.59	0.65	0.72
	50	2.10	2.32	2.50	0.95	1.10	1.25
	55	3.47	3.83	4.27	2.69	2.98	3.32
	60	6.71	7.32	7.67	5.31	5.62	6.01

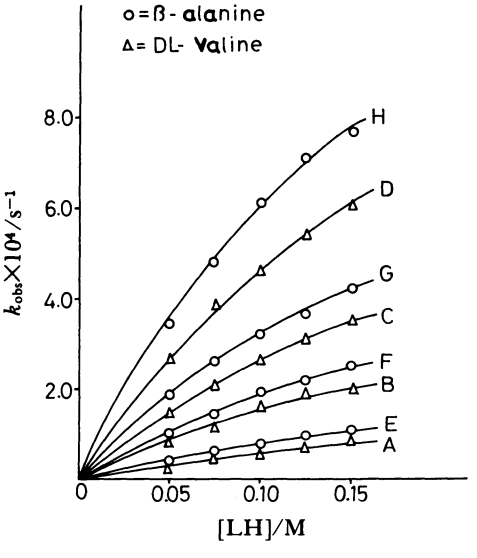

Fig. 2. Effect of ligand concentration (LH) on rate constant (k_{obs}) at different temperatures A) 45 °C, B) 50 °C, C) 55 °C, D) 60 °C; E) 45 °C, F) 50 °C, G) 55 °C, and H) 60 °C.

keeping Complex 1 (0.005 M), pH (4.2) and ionic strength (0.03 M) fixed. The result shown in Table 1 exhibits that for both β-alanine and DL-valine the rate increases with the increase of ligand concentration and reaches a limiting value at higher ligand concentration (Fig. 2). This is due to completion of ion pair formation with the substrate complex ion and amino acid ligands through its negative end. Actually when the zwitterionic amino acid ligand is brought to react with the triply charged substrate complex ion it occupies the near vicinity of complex ion replacing the solvent molecule. Thus an ion pair species is formed in a very rapid process. Then ligand molecule occupies the site vacated by the leaving water molecule in a slower rate determining step. Now increase in ligand concentration increases the concentration of ion pair in the solution and lastly at certain ligand concentration ion pair formation is completed. Further addition of ligand increases it's amount in bulk solution.

The following scheme commensurating the above fact can be set up to explain the variation of rate with ligand concentration.

$$cis\text{-}[Co(en)_2(H_2O)_2]^{3+} + LH \overset{K_E}{\rightleftharpoons} \underset{IP}{cis\text{-}[Co(en)_2(H_2O)_2]^{3+}\cdot LH}$$

$$cis\text{-}[Co(en)_2(H_2O)_2]^{3+}\cdot LH \xrightarrow{k_a} cis\text{-}[Co(en)_2(H_2O)(LH)]^{3+} + H_2O$$

Considering ion pair equilibrium (K_E) and rate determining step (k_a) a familiar rate expression has been established

$$\frac{d[Co(en)_2LH^{3+}]}{dt} = \frac{k_aK_E[Co(en)_2(H_2O)_2^{3+}]_T[LH]}{1 + K_E[LH]}$$

$$= k_{obs}[Co(en)_2(H_2O)_2^{3+}] \quad (2)$$

Now

$$k_{\text{obs}} = \frac{k_a K_E[\text{LH}]}{1 + K_E[\text{LH}]} \tag{3}$$

or

$$1/k_{\text{obs}} = 1/k_a + 1/k_a K_E[\text{LH}] \tag{4}$$

Here $[\text{Co(en)}_2(\text{H}_2\text{O})_2{}^{3+}]_T$=concentration of total unreacted complex, and [LH] represents the concentration of β-alanine or DL-valine in their respective zwitterionic forms.

From Eq. 3 plot of $1/k_{\text{obs}}$ vs. 1/[LH] at a constant pH gives a straight line (Fig. 3) with an intercept $1/k_a$ and slope $1/k_a K_E$. The values of k_a are given in Table 2. K_E values were found to be more or less temperature independent, but at a given temperature K_E values increase with the increase in organic component i.e. lowering of dielectric constant of the medium, range from 1.8 to 6.2 M^{-1}. In proposing the above scheme it was resonably assumed that under experimental conditions only cis-diaquo complex is involved in the reaction.

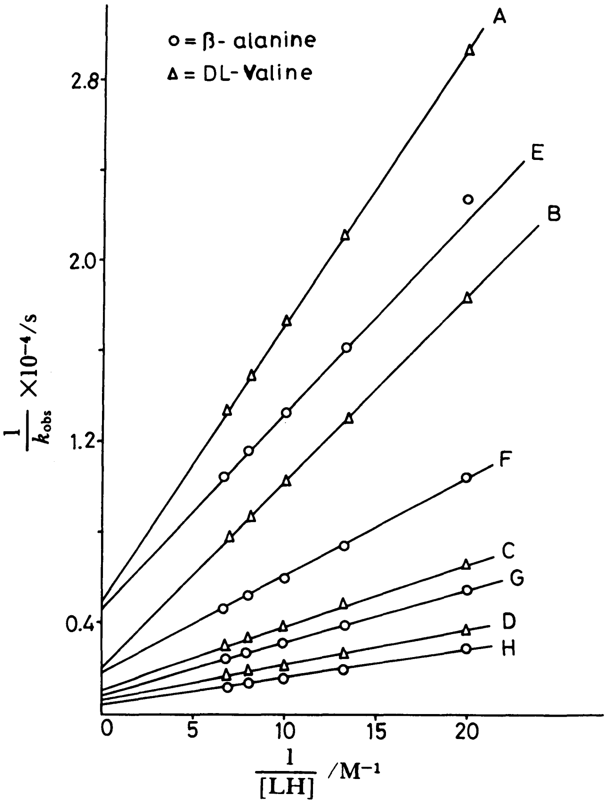

Fig. 3. Plot of $1/k_{\text{obs}}$ vs. 1/[LH] at different temperatures A) 45 °C, B) 50 °C, C) 55 °C, and D) 60 °C; E) 45 °C, F) 50 °C, G) 55 °C, and H) 60 °C.

iv) Effect of Ionic Strength on Rate Constant. At fixed [Complex 1] (0.005 M), [ligand] (0.075 M) and pH 4.2 the ionic strength of the medium was varied by adding (a) NaNO_3 and (b) NaClO_4. It is observed that at 55 °C k_{obs} values increase with the increase in $\text{NO}_3{}^-$ concentration. The values of $k_{\text{obs}}(\times 10^4\,\text{s}^{-1})$ at 55 °C are 2.61, 2.93, 3.11, 3.43, and 3.93 (for β-alanine) and 1.90, 2.10, 2.98, 3.64, and 4.60 (for DL-valine) at different ionic strengths 0.03, 0.1, 0.25, 0.5, and 1.0 M respectively. Whereas $\text{ClO}_4{}^-$ ion cannot make any change in the k_{obs} values. Considering the net charge of the zwitterionic amino acid ligands being zero the reaction rate should have been independent of ionic strength of the medium,[23] hence the variation of ionic strength made by adding $\text{ClO}_4{}^-$ did not produce any change in rate constant values. But it was shown by Brown and Harris[2] that $\text{NO}_3{}^-$ has greater tendency to attack coordinated water molecule rather than water molecules attached to the ligands and this facilitates Co–OH_2 bond fission and thus increase of rate occurs.

v) Effect of Variation of Dielectric Constant on Rate Constant. Effect of solvent composition on the water replacement reactions of *cis*-$[\text{Co(en)}_2(\text{H}_2\text{O})_2]^{3+}$ with amino acids was studied in three different ethanol–water mixtures (10, 20, and 30% v/v). Table 2 shows that at a particular temperature the values of interchange rate constant k_a decrease with the increase

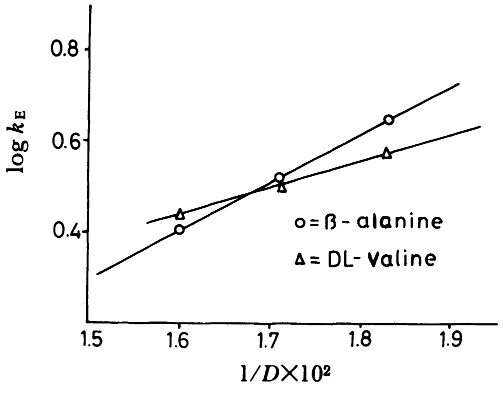

Fig. 4. Plot of log K_E vs. 1/D at 55 °C.

Table 2. Values of k_a at Different Temperatures in Various Ethanol–Water Mixtures

Temp	$k_a \times 10^4/\text{s}^{-1}$					
	β-Alanine			DL-Valine		
°C	% of ethanol (v/v)			% of ethanol (v/v)		
	10	20	30	10	20	30
45	3.13	2.77	2.12	2.97	2.51	2.01
50	7.24	6.35	5.18	6.85	5.63	5.00
55	12.30	11.31	10.10	11.90	10.10	9.52
60	25.30	22.81	21.30	25.10	22.30	20.00

of organic component of the medium. But reverse is true for K_E values ranging from 1.8 to 6.2 M^{-1}. Actually this is in good agreement with the ion pair formation that lowering of dielectric constant i.e., increases in organic component of the medium increases the forces of attraction between two ions, which favors the ion pair formation (Fig. 4).

According to the electrostatic theory, the dependence of the rate constant of the ion dipole typed reaction on the dielectric constant of the medium is best represented by the Laidler–Eyring equation.[23] In our case considering the total charge on the amino acid ligand is zero the Laidler–Eyring equation can be represented in a simplified way.

$$\frac{d\ln k_a}{d(1/D)} = \frac{e^2Z^2}{2kT}(1/r_1 - 1/r_2) \tag{5}$$

Here, Z is the charge on the complex ion, r_1 and r_2 represent the effective radii of the ion pair in the ground state and in activated state (activated ion pair) respectively, k=Boltzmann constant, T=temperature in absolute degree and D represents the changing dielectric constant. It is seen from Eq. 5, that if $r_2 < r_1$, plot of ln k_a vs. $1/D$ will give a straight line having a negative slope. Now for dissociative interchange process one water molecule is lost in the activated state consequently size of the activated species is lowered i.e. r_2 becomes smaller than r_1. Had it been followed an associative path, the elongation of metal–water bond in the activated states increases the size of the activated species i.e. r_2 becomes larger than r_1. In practice we got a good straight line by ploting ln k_a against $1/D$ with a small negative slope (Fig. 5). This is because r_1 and r_2 do not differ markedly since size of lost water molecule is small in comparison to the large complex ion. Another equation[13] which shows the relation between the rate constant of the ion-dipole reaction and dielectric constant of the medium is as follows:

$$\frac{d\ln k_a}{d(1/D)} = -\frac{Z^2e^2}{kTr_0^2}\mu_{LH}\cos\theta \tag{6}$$

Here μ_{LH} is the dipole moment of the amino acid ligand, θ is the angle which the negative end of the dipole makes with the line joining the center of the dipole to the complex ion. r_o is the critical ion-dipole distance which is more or less the same in ground state or activated state as stated earlier. In case of dissociative interchange mechanism one water molecule is dissociated from the metal ion and as a result metal ion attracts the negatively charged oxygen atom in carboxylate group of the amino acid ligand towards on itself. Consequently in this case the value of angle θ cannot exceed the value 90° and thus plot of ln k_a against $1/D$ always gives a straight line with a negative slope. In case of associative interchange process θ may be greater than 90° because complete detachment of water molecule dose not occur in activated state, which increases the steric effect that pushes the negative end of the dipole far from its equilibrium position. However, the small difference obtained in the values of k_a (Table 2) may be due to other non-electrostatic solvent–solute interaction. An interesting point to be noted here is that the values of k_{obs} (Table 1) increase with the increase in organic component of the medium. This is due to increasing effect of K_E on k_{obs} is larger than that of opposite effect of k_a on k_{obs} (Eq. 4).

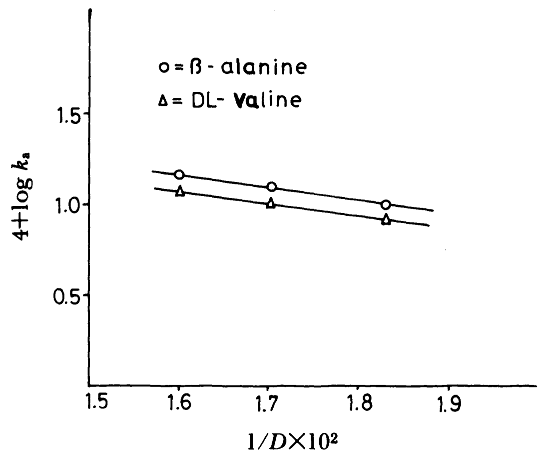

Fig. 5. Plot of log k_a vs. $1/D$ at 55 °C.

vi) **Effect of Temperature on Rate Constant.** The reactions were studied at four different temperatures for media of three different dielectric constants. Activation parameters were calculated by using the Eyring equation and the data obtained were checked by a least squares method and compared with data shown for isotopic water exchange process[25] and other substitution reactions (Table 3). It is seen from Table 3 that the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values increase with as the dielectric constant of the medium decreases.

Table 3. Values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Different Ethanol–Water Mixtures

% of ethanol (v/v)	β-Alanine		DL-Valine	
	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
	kcal mol^{-1}	cal deg^{-1}	kcal mol^{-1}	cal deg^{-1}
10	26.2	13.3	25.8	12.2
20	27.7	14.1	27.4	13.9
30	30.0	18.1	29.1	15.7

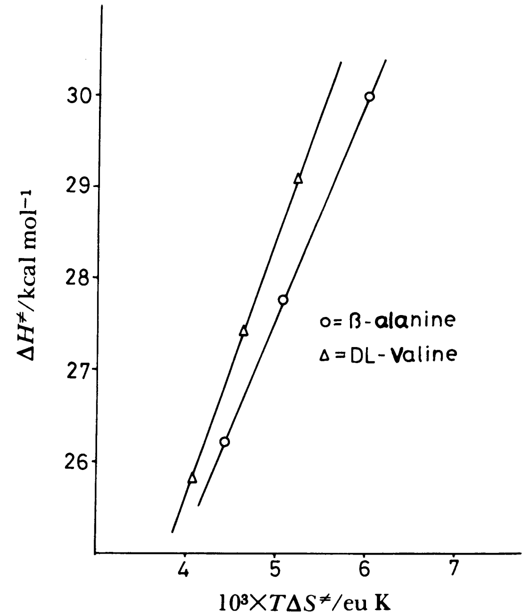

Fig. 6. Isokinetic plot of ΔH^{*} vs. $T\Delta S^{*}$.

Though the reactions are performed in water rich media, but crowding of non-polar solvent molecule in the outersphere zone diminishes the rate of $Co–OH_2$ bond dissociation and thus higher activation energy is required, which is reflected from Table 3. Again increase in organic component effects the solvation of reacting species as well as activated species. Increase in $\Delta S^{\neq}$ values observed is mainly due to change in solvation of the system concerned. Interestingly plots of $\Delta H^{\neq}$ vs. $T\Delta S^{\neq}$ are linear for both the water replacement reactions (Fig. 6). It may be inferred that the similar transition states are formed in the studied range of the composition of the solvent pair.

Conclusion

Basing the above facts a dissociative interchange mechanism (I_d) has been suggested in which complex *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ first forms an ion pair with the incoming amino acid ligands viz. *β*-alanine and DL-valine in a very rapid step, then slow replacement of water molecule occurs through a dissociative pathway in which amino acid ligand takes the position vacated by leaving water molecule.

We are thankful to CSIR for senior research fellowship to DC.

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