

Acid-base equilibria of some salicylatopentaminocobalt(III) ions in mixed solvent media: An attempt to study molecular recognition

Anadi C Dash*, Kishore C Jena & Achyuta N Acharya[†]

Department of Chemistry, Utkal University, Bhubaneswar 751 004, India

Received 8 April 1994; revised and accepted 20 July 1994

The study of the acid-base equilibria of $cis-[Co(en)_2(RNH_2)_2O_2CC_6H_4OH]^{2+}$ ($R = H, CH_3, CH_3CH_2$) in methanol-water, propan-2-ol-water, *tert*-butanol-water, acetone-water, and ethylene glycol-water ($0 \leq \text{vol \% organic solvent} \leq 70$) are reported at 25°C. The transfer free energy of the phenol form relative to that of phenoxide form of the complexes, where transfer occurs from water to the mixed solvents, have been evaluated. Solubility studies for the sparingly soluble dithionate salt of the phenol form of these complexes have been made in methanol-water media at 25°C and the transfer free energy of the phenol and phenoxide species (relative to water) have been assessed. Results highlight the electrostatic and nonelectrostatic medium effects on the solvation of the phenol and phenoxide species of the complexes. The transfer free energy data suggest that the complex ions recognise the cosolvent molecules in their Gurney cosphere via both coulombic and hydrophobic interactions.

The free energy change for any chemical reaction is a thermodynamic criterion of molecular recognition. Solvation of reactants and products affects their free energies and hence the overall free energy change of the associated equilibrium¹⁻³. In a mixed aquo-organic solvent medium, the solute species (i.e. reactants and products) depending on their charges, hydrophobicity and hydrogen bonding propensities can interact with the solvent components to different degrees^{4,6}. The solvent structure and composition in the cosphere of the solute species may thus not be the same as in the bulk phase of the mixed solvent media. The resulting preferential solution effect, a measure of molecular recognition, is likely to be reflected in the overall free energy change for a process in which the dissolved solute participate. Both electrostatic and nonelectrostatic factors will, however, govern the free energy changes.

We have chosen a standard acid-base reaction of some *cis*-(amine)bis(ethylenediamine)(salicylato)cobalt(III) substrates and studied the equilibrium (see Eq. (1)) in methanol-water, isopropanol-water, *tert*-butanol-water, ethylene glycol-water and acetone-water media. The aim was (i) to examine the solvent effects on the acid-base equilibrium and (ii) to know about the relative solvational feature of the phenol and phenoxide species of the sub-

strates in these mixed solvent media by assessing their transfer free energies.

Materials and Methods

The *cis*-(amine)bis(ethylenediamine)(salicylato)cobalt(III) diperchlorates, $cis-[(RNH_2)(en)_2CoO_2-CC_6H_4(o)OH](ClO_4)_2$ ($R = H, CH_3, CH_3CH_2$) were prepared and purity checked by analytical and UV-visible spectral data as reported earlier^{7,8}. The sparingly soluble dithionate salts of these complexes were prepared by the double decomposition of their perchlorate salts with sodium dithionate. These samples were at least twice crystallized from warm water, washed with ethanol followed by ether and dried over fused calcium chloride. The purity was checked by analysis of cobalt. Analytical grade reagents were used for equilibrium studies. Methanol (MeOH), propan-2-ol (Pr^oOH), *tert*-butanol (Bu^oOH), ethylene glycol (EG) and acetone (AC) were of >99% purity grade. These solvents were kept over molecular sieve and distilled before solvent mixtures were prepared in volume percent. Alkali was standardised against potassium hydrogen phthalate.

All absorbance measurements were made on a Jasco 7800 recording spectrophotometer using 10 mm matched quartz cells.

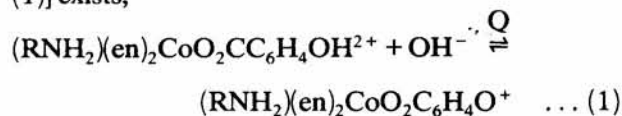
Equilibrium measurements

The acid base equilibrium was studied spectrophotometrically at 310 nm. The absorbance of a

[†]Present address: Lecturer in Chemistry, Institute of Textile Technology, Choudwar, Cuttack 754 025

known concentration ($\approx 4.6 \times 10^{-4}$ mol dm $^{-3}$) of any complex in aquo-organic solvent media was measured at different $[\text{NaOH}]_{\text{T}}$ and at $[\text{HClO}_4]_{\text{T}} = 0.10$ mol dm $^{-3}$ ($1 \leq \text{pH} \leq 13$); ionic strength was maintained constant at 0.10 mol dm $^{-3}$ using NaClO_4 wherever necessary. Typical plots of absorbance versus $[\text{OH}^-]_{\text{T}}$ (see Fig. 1) indicate that ionisation of the phenol group is complete at $[\text{OH}^-]_{\text{T}} \geq 0.05$ mol dm $^{-3}$. Thus the absorbance in 0.10 mol dm $^{-3}$ HClO_4 and at $[\text{OH}^-]_{\text{T}} \geq 0.05$ mol dm $^{-3}$ was taken to be that of the phenol and phenoxide forms of the complex respectively. The base hydrolysis of the complexes were too slow to affect measurements^{8,9}. However, zero time extrapolated absorbance data were taken to calculate the equilibrium constant (Q) as given below.

At any value of $[\text{OH}^-]_{\text{T}}$ when equilibrium between the phenol and phenoxide forms [see (Eq. 1)] exists,



the absorbance of the complex (for cell length = 1 cm) is given by Eq. (2)

$$A = \epsilon_{\text{obs}}a = \epsilon_1(a-x) + \epsilon_2x \quad \dots (2)$$

where ϵ_1 and ϵ_2 denote the molar extinction coefficients of the phenol and phenoxide forms of the complexes respectively; $a = [\text{complex}]_{\text{T}}$ and x is the concentration of the phenoxide species, ϵ_1 and ϵ_2 were taken to be ϵ_{obs} at $[\text{H}^+] = 0.10$ mol dm $^{-3}$ and at $[\text{OH}^-]_{\text{T}} \geq 0.05$ mol dm $^{-3}$ respectively to calculate x using Eq. (2), Q was then calculated using Eq. (3) which assumes $f_{\text{OH}^-} = f_{\text{RO}^-}$

$$Q = \left[\frac{x}{(a-x)([\text{OH}^-]_{\text{T}} - x)} \right] \cdot \frac{1}{f_{\text{ROH}^{2+}}} \quad \dots (3)$$

where $f_{\text{ROH}^{2+}}$ denotes the activity coefficient of the phenol species. The activity coefficient was calculated from the Debye Huckel relationship (Eq. 4)

$$\log f_z = -AZ^2I^{1/2}/(1 + BaI^{1/2}) \quad \dots (4)$$

with $A = 1.8246 \times 10^6 / (D_s \cdot T)^{3/2}$, $B = 50.29 \times 10^8 / (D_s \cdot T)^{1/2}$, $a = 5 \text{ \AA}$ where D_s denotes bulk dielectric constant of the medium¹⁰ and T is temperature in absolute scale. Values of Q and the standard free energy change ($\Delta G^0 = -RT \ln Q$) are collected in Table 1.

The solubilities of the sparingly soluble dithionate salts of the complexes were measured spectrophotometrically (310 nm) at 25°C in MeOH-H $_2$ O

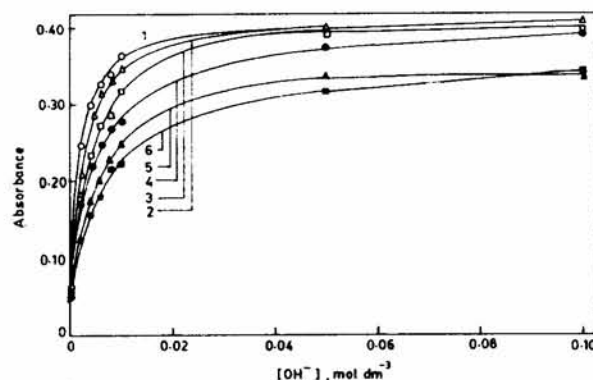


Fig. 1—Absorbance versus $[\text{OH}^-]/\text{mol dm}^{-3}$ plot for $\text{cis}-[(\text{en})_2(\text{CH}_3\text{NH}_2)\text{CoO}_2\text{CC}_6\text{H}_4\text{OH}]^{2+}$ ($4.6\text{--}4.8 \times 10^{-4}$ mol dm $^{-3}$) in different compositions of (v/v) % MeOH: 1, 0%; 2, 20%; 3, 40%; 4, 50%; 5, 60%; 6, 70%.

Table 1—Calculated values of standard free energy $\Delta G^0/\text{kJ mol}^{-1}$ for NH_3 , CH_3NH_2^+ and $\text{CH}_3\text{CH}_2\text{NH}_2^{++}$ complexes at 25°C in mixed solvent media

Vol % Organic solvent	ΔG^0 (kJ mol)				
	MeOH	Pr t -OH	Bu t -OH	AC	EG
0	-19.4(-18.8)[-18.6]	-19.4	-19.4(-18.8)[-18.6]	-19.4	-19.4
10.0	-17.7(-18.2)[-18.5]	-19.7	-19.1(-19.4)[-18.9]	-19.3	-18.0
20.0	-18.6(-18.2)[-18.2]	-20.4	-19.7(-19.8)[-19.6]	-18.5	-17.7
30.0	-18.1(-18.0)[-17.6]	-20.8	-20.8(-19.6)[-20.1]	-19.6	-16.8
40.0	-17.7(-17.2)[-17.2]	-21.5	-21.6(-20.1)[-20.8]	-20.9	-16.7
50.0	-17.6(-17.3)[-16.9]	-22.5	-23.4(-22.6)[-22.1]	-21.2	-16.0
60.0	-17.7(-17.2)[-16.8]	-23.7,	—	—	-15.8
70.0	-17.8(-17.3)[-16.5]	—	—	—	—

[†]Values for CH_3NH_2 complexes ()

[‡]Values for $\text{CH}_3\text{CH}_2\text{NH}_2$ complexes []

media. The molar extinction coefficients of the complexes were independent of the solvent composition (see footnote of Table 2). The solubility data as well as the standard free energy change ($\Delta G_{\text{sol}}^0 = -2RT \ln Sf^{\pm 2}$, $f^{\pm 2} = f_{\text{ROH}^{2+}} \cdot Xf_{\text{S}_2\text{O}_8^{2-}}$, S-solubility of the complex salt) are given in Table 2.

Results and Discussion

It is worth noting that the equilibrium constant Q is sensitive to the medium properties for a given complex as also to the nature of the complex, as the nonlabile amine ligand is varied. The electrostatic effect remaining the same, the small but definite changes in Q with variation of the amine ligand in a given solvent demonstrates the significance of noncoulombic factors such as hydrophobic interactions and solvent structure which are likely to mediate the solvation of the complex ions and hence the equilibrium constant.

A quantitative assessment of the solvation of the complexes can be had in terms of the transfer

free energy changes. Since $\Delta G^0 = \bar{G}^0(\text{RO}^+) - \bar{G}^0(\text{OH}^-) - \bar{G}^0(\text{ROH}^{2+})$, where $\bar{G}^0(i)$ denotes the standard free energy of a species i , the transfer free energy of RO^+ (phenoxide species) relative to that of the phenol species (ROH^{2+}), when transfer occurs from water (w) to the mixed solvent (s) can be written as Y as given in Eq. (5)

$$Y = [\Delta G_i^0(\text{RO}^+) - \Delta G_i^0(\text{ROH}^{2+})]_{(s-w)} \\ = [\Delta G_i^0(\text{OH}^-)]_{(s-w)} - RT \ln Q_s/Q_w \quad \dots (5)$$

$[\Delta G_i^0(\text{OH}^-)]_{(s-w)}$ were taken from literature^{11,12}. Values of Y (see Table 3) reflect that it is least affected by EG-water although dielectric constant varies in the range 78.6-59 (for vol % EG = 0-60). Despite this fact a minimum for Y discernible at 40 vol % EG (see Table 3) might be related to the solvent structure enforced differential solvation of the phenoxide and phenol form of the salicylatoaminocobalt(III) complexes. It is worth noting that Y is positive, $[\Delta G_i^0(\text{RO}^+)]_{(s-w)} > [\Delta G_i^0(\text{ROH}^{2+})]_{(s-w)}$, for all monohydric alcohols

Table 2—Solubility data and calculated values of $[\Delta G_i(\text{ROH}^{2+})]_{(s-w)}$ and $[\Delta G_i(\text{RO}^+)]_{(s-w)}$ at 25°C

Vol % MeOH	$10^4 S$ (mol dm ⁻³)	ΔG_{sol}^0 (kJ mol ⁻¹)	$[\Delta G_i(\text{ROH}^{2+})]_{(s-w)}$ (kJ mol ⁻¹)	$[\Delta G_i(\text{RO}^+)]_{(s-w)}$ (kJ mol ⁻¹)
<i>cis</i> -[(en) ₂ (NH ₃)CoO ₂ CC ₆ H ₄ (<i>o</i>)OH] ²⁺				
0	1.734	0	0	0
10	1.048	2.4	-0.5	1.2
20	0.767	3.9	1.8	1.0
30	0.576	5.3	0.9	0.4
40	0.448	6.5	-1.0	0.7
50	0.387	7.3	-4.0	-1.7
60	0.314	8.3	-5.7	-2.3
<i>[cis</i> -(en) ₂ (CH ₃ NH ₂)CoO ₂ CC ₆ H ₄ (<i>o</i>)OH] ²⁺				
0	2.346	0	0	0
10	1.934	1.0	-2.0	-1.3
20	1.276	2.9	0.8	1.4
30	1.058	3.9	-0.6	0.1
40	0.910	4.7	-1.2	-2.80
50	0.787	5.4	-6.0	-4.0
60	0.656	6.3	-7.7	-3.2
<i>cis</i> -[(en) ₂ (CH ₃ CH ₂ NH ₂)CoO ₂ CC ₆ H ₄ (<i>o</i>)OH] ²⁺				
0	1.117	0	0	0
10	0.852	1.3	-1.6	-1.5
20	0.748	2.0	-0.1	0.2
30	0.575	3.3	-1.2	-0.3
40	0.452	4.4	-3.1	-1.5
50	0.323	6.1	-5.2	-1.7
60	0.232	7.7	-6.3	-2.7

(a) $\Delta G_{\text{sol}}^0 = -2RT \ln Sf^{\pm 2}$

(b) Based on $[\Delta G_i(\text{S}_2\text{O}_8^{2-})]_{(s-w)}$ (kJ mol⁻¹) = 2.9, 2.1, 4.4, 7.5, 11.3 and 14.0 at 10, 20, 30, 40, 50 and 60 vol % MeOH at 25°C¹⁰.

and relatively more so for acetone. It also increases with increasing proportion of the non-aqueous component. Both electrostatic and nonelectrostatic effects contribute to Y ($T_{\text{overall}} = Y_{\text{el}} + Y_{\text{nonel}}$). The plots of Y versus $10^2/D_s$ for $(\text{en})_2(\text{NH}_3)\text{CoO}_2\text{CC}_6\text{H}_4\text{OH}^{2+}$ (see Fig. 2) are essentially nonlinear and clearly reflect the individuality of cosolvents. The plots of Y versus $10^2/D_s$ for NH_3 , CH_3NH_2 and $\text{CH}_3\text{CH}_2\text{NH}_2$ complexes for $\text{MeOH-H}_2\text{O}$ and $\text{Bu}^i\text{-OH-H}_2\text{O}$ media show little dependence on the nature of the nonlabile amine group as expected. The solvent dependence of Y at constant dielectric constant (i.e. at $D_s = 60$, see Fig. 3) demonstrates the variation of the destabilising effect of the medium on the complex species and this must be attributed to Y_{nonel} , the nonelectrostatic component of Y_{overall} . It appears that the species ROH^{2+}

and RO^+ recognise the organic cosolvent molecules through both coulombic and noncoulombic (hydrophobic) interactions.

The solubility data for the complexes in $\text{MeOH-H}_2\text{O}$ media combined with the transfer free energy data for $\text{S}_2\text{O}_6^{2-}$ (based on TPTB assumption for $\text{MeOH-H}_2\text{O}$ media)¹² yielded the values of $[\Delta G_t^0(\text{ROH}^{2+})]_{\text{s-w}}$

$$[\Delta G_t^0(\text{sol})]_{\text{s-w}} = [\Delta G_t^0(\text{ROH}^{2+})]_{\text{s-w}} + [\Delta G_t^0(\text{S}_2\text{O}_6^{2-})]_{\text{s-w}}$$

Combining these values with that for Y (see Table 3), we also obtained the transfer free energy of the phenoxide species, $[\Delta G_t^0(\text{RO}^+)]_{\text{s-w}}$. These data

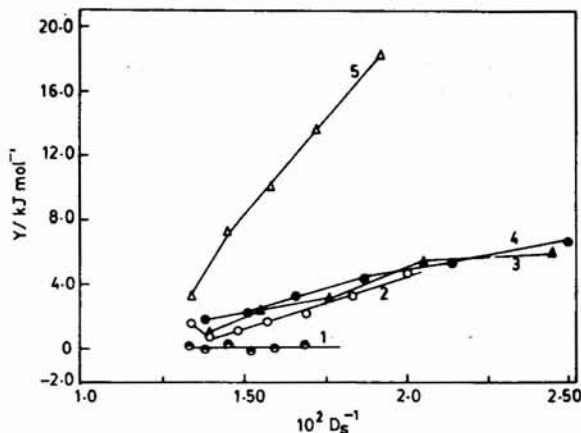


Fig. 2—Plot of Y (kJ mol^{-1}) versus $10^2/D_s$ for $\text{cis}-(\text{en})_2(\text{NH}_3)\text{CoO}_2\text{CC}_6\text{H}_4\text{OH}^{2+}$ in different aquo-organic solvent media: 1, EG; 2, MeOH; 3, $\text{Bu}^i\text{-OH}$; 4, $\text{Pr}^i\text{-OH}$; 5, AC.

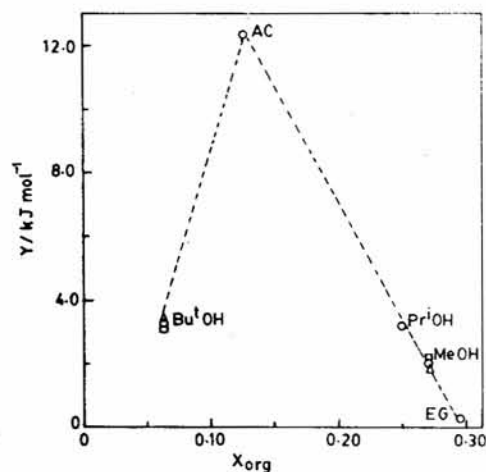


Fig. 3—Plot of Y (kJ mol^{-1}) versus X_{org} under isodielectric conditions ($D_s = 60$) at 25°C , data points refer to mole fraction of the organic component; complex = $\text{cis}-(\text{en})_2(\text{X})\text{CoO}_2\text{CC}_6\text{H}_4\text{OH}^{2+}$: for $\text{X} = \text{NH}_3$ (O), CH_3NH_2 (Δ) and $\text{CH}_3\text{CH}_2\text{NH}_2$ (\square).

Table 3—Calculated values of relative transfer free energy for NH_3 complex $Y = [\Delta G_t^0(\text{RO}^+) - \Delta G_t^0(\text{ROH}^{2+})]_{\text{s-w}}$ (kJ mol^{-1}) at 25°C in mixed solvents

Vol % Organic solvent	Y^a (kJ mol^{-1})				
	MeOH	$\text{Pr}^i\text{-OH}$	$\text{Bu}^i\text{-OH}$	AC	EG
10	1.7(0.7)[0.08] ^{††}	1.8	1.1(0.3)[0.6]	3.3	0.3
20	0.8(0.6)[0.3]	2.3	2.5(1.8)[1.8]	7.4	0.09
30	1.3(0.7)[0.9]	3.2	3.9(4.6)[3.9]	10.2	0.4
40	1.7(1.6)[1.6]	4.3	5.5(6.4)[5.5]	13.6	-0.03
50	2.3(2.0)[2.5]	5.4	6.0(6.2)[6.5]	18.2	0.1
60	3.4(3.2)[3.6]	6.6	— — —	—	0.4
70	4.7(4.5)[5.9]	—	— — —	—	—

[†]Values for CH_3NH_2 complexes ()

^{††}Values for $\text{CH}_3\text{CH}_2\text{NH}_2$ complexes []

for MeOH-H₂O media for all the three complexes are collected in Table 2. A clear distinction in the interaction of the phenol and phenoxide species (having same size but differing in charge bearing centres) with MeOH-H₂O media is now evident, the ROH²⁺ species are relatively more stabilised in MeOH-H₂O media with increasing hydrophobicity of the nonlabile amine function. The solvent stabilisation of ROH²⁺ species also increases on making the medium more non-aqueous. The observed behaviour of the phenoxide species in relation to solvent stabilisation (see values of $[\Delta G_{\text{f}}^{\circ}(\text{RO}^+)]_{\text{s-w}}$ in Table 2) reflect that specific hydrogen bonding interaction of the medium with the phenoxide moiety plays a vital role.

Acknowledgement

ACD is thankful to the CSIR, New Delhi for financial support. KCJ is thankful to the D.S.T., Govt. of Orissa, for a junior research fellowship. The authors are grateful to Dr. John Burgess, Department of Chemistry, University of Leicester, Leicester, U.K., for making the transfer free energy data of S₂O₆²⁻ available.

References

- 1 Dash A C, Dash N, Pradhan J P & Das P K, *J chem Soc Faraday Trans*, 86 (1990) 2215.
- 2 Dash A C & Pradhan J P, *Int J chem Kinet*, 24 (1992) 155; *J chem Soc Faraday Trans* 1, 84 (1988) 2387.
- 3 Dash A C & Dash N, *Int J chem Kinet*, 22 (1990) 1237; *J chem Soc Faraday Trans* 1, 83 (1987) 2505; *J chem Soc Faraday Trans*, 84 (1988) 25.
- 4 Al-Alousy A, Alshehri S, Blandamer M J, Blundell N J, Burgess J, Cowles H J & Radulovic S, *J chem Soc Faraday Trans*, 89 (1993) 1041.
- 5 Armand F, Sakuragi H & Tokumanu K, *J chem Soc Faraday Trans*, 89 (1993) 1021.
- 6 Y Marcus, *Ion solvation*, (Wiley, New York), 1985, Chapt 7.
- 7 Dash A C & Dash M S, *J inorg nucl Chem*, 38 (1976) 576.
- 8 Pradhan G C, *Trans met Chem*, 17 (1992) 443.
- 9 Dash A C & Mohanty B, *J inorg nucl Chem*, 40 (1978) 309.
- 10 Ref 6, page 188.
- 11 Burgess J & Blandamer M J, *Trans met Chem*, 13 (1985) 1.
- 12 The transfer free energy data of S₂O₆²⁻ for MeOH-H₂O media are based on TPTB assumption (available in Kan-al's thesis, University of West Indies, Jamaica, 1993), data through Dr John Burgess, Department of Chemistry, University of Leicester, Leicester, UK.