

Thermodynamics of Ionisation and Complex Formation of Pyrocatechol Violet with Copper(II), Nickel(II) and Zinc(II) using Potentiometric Technique

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The complexation of copper, zinc and nickel with pyrocatechol violet (PCV) was investigated using potentiometric method. The ionisation of pure PCV and the formation constants of metal-PCV complexes are obtained from potentiometry at five temperatures; 25, 30, 35, 40 and 45° in different aqueous solutions of fixed ionic strengths ($I=0.04, 0.07, 0.11$ and 0.15 mol dm^{-3}) using NaClO_4 . Thermodynamic equilibrium constants (at $I=0$) are also reported. The data are discussed in the light of structural effects, proton transformation and hydrogen bonding effects. Thermodynamic parameters associated with the ionisation and the complexation equilibria have been evaluated. Thermodynamic metal gradient (B) was derived to discuss the thermodynamic characteristics of metal ion complexes.

Hydrogen bonding and proton transformation play important role¹ in determining the reactivity of compounds containing OH, COOH and SO_3 groups. In an earlier investigation², we discussed the effects of the functional groups on the reactivity. In the present communication, we selected a compound which contains four OH groups and one SO_3 group, namely, pyrocatechol violet (PCV). This would enable studying the effect of both hydrogen bonding and proton transformation on its ionisation.

Pyrocatechol violet was studied by Mushran *et al.*³ but without determination of its ionisation constants. Lakhani⁴ studied mixed ligand chelates of rare earth with pyrocatechol violet in aqueous solutions. Neilboer and McBryde⁵ discussed the linearity between protonation constants of derivatives of selected reference compounds and the corresponding stability constants of these derivatives with given metal using the equation,

$$\log K_{\text{ML}} = B \log K_{\text{MsL}} + [\log K_{\text{MLo}} - B \log K_{\text{MsLo}}] \quad (1)$$

However, in view of the relation between standard free energy change and stability or protonation constants, the previous equation can be expressed in terms of free energy,

$$\Delta G_{\text{ML}}^{\circ} = B \Delta G_{\text{MsL}}^{\circ} + [\Delta G_{\text{MLo}}^{\circ} - B \Delta G_{\text{MsLo}}^{\circ}] \quad (2)$$

where $\Delta G_{\text{ML}}^{\circ}$ is the standard free energy of complexation process at any temperature, $\Delta G_{\text{MsL}}^{\circ}$ the algebraic summation of standard free energies for all protonation constants at any temperature, $\Delta G_{\text{MLo}}^{\circ}$ the standard free energy of complexation process at 25°, $\Delta G_{\text{MsLo}}^{\circ}$ the algebraic summation of standard free energies of protonation constants at 25°, and B the rate of change of stability standard free energy of complex ML at different temperatures of the metal ion M with the protonation standard free

energy of the related ligand L at different temperatures, i.e. thermodynamic metal gradient. Then, we shall study the linearity between $\Delta G_{\text{ML}}^{\circ}$ against $\Delta G_{\text{MsL}}^{\circ}$. In this manner and by that new approach, we can use the values of B to discuss the thermodynamic characteristics of metal ion complexes.

Results and Discussion

PCV has four ionisation constants (due to the presence of four hydroxyl groups). The potentiometric data were analysed by computer using the following equations⁶ for calculation of $\text{p}K_1$ and $\text{p}K_4$ (where the values of $\text{p}K$'s are not comparable, $\text{p}K_1 \gg \text{p}K_4$),

$$\text{p}K_1 = \text{pH} + \log \frac{C_t - C_{\text{NaOH}} - C_{\text{H}^+} + C_{\text{OH}^-}}{C_{\text{NaOH}} + C_{\text{H}^+} - C_{\text{OH}^-}} + \frac{AI^{\frac{1}{2}}}{1 + a^{\circ}BI^{\frac{1}{2}}} \quad (3)$$

$$\text{p}K_4 = \text{pH} + \log \frac{4C_t - C_{\text{NaOH}} - C_{\text{H}^+} + C_{\text{OH}^-}}{C_{\text{NaOH}} - (3)C_t + C_{\text{H}^+} - C_{\text{OH}^-}} + \frac{3AI^{\frac{1}{2}}}{1 + a^{\circ}BI^{\frac{1}{2}}} \quad (4)$$

where C_t is the concentration of the acid originally taken allowing for volume changes as a result of the addition of titrant, C_{NaOH} the total concentration of standard alkali added including that used in the neutralisation of stronger group and C_{H^+} the concentration of hydrogen ion in solution, where

$$-\log C_{\text{H}^+} = \text{pH} - \frac{AI^{\frac{1}{2}}}{1 + a^{\circ}BI^{\frac{1}{2}}} \quad (5)$$

and C_{OH^-} is the concentration of hydroxide ion, where

$$-\log C_{OH^-} = pK_w - pH + \frac{AI^{\frac{1}{2}}}{1 + a^\circ BI^{\frac{1}{2}}} \quad (6)$$

(pK_w is the ionic product of water at the corresponding temperature), I is the ionic strength of the solution, A and B are Debye-Hückel constants, and a° is the closest distance of approach. But for calculation of pK_2 and pK_3 (there is an overlap in pK 's values), the Speakman equation⁷ is recommended,

$$a_{H^+} \left(\frac{1-\bar{h}}{2-\bar{h}} \right) K_2 + K_2 K_3 = \frac{a_{H^+}^2 \bar{h}}{2-\bar{h}} \quad (7)$$

where, $a_{H^+} = \log^{-1} pH$ (8)

$$\bar{h} = \frac{C_{NaOH} + C_{H^+} - C_{OH^-}}{C_t} \quad (9)$$

where K_2 and K_3 are the second and third ionisation constants.

The stability constants of metal ion complexes of Cu, Zn and Ni with PCV are calculated by Irving-Rossotti equation⁸,

$$\bar{n} + \sum_1^N (\bar{n} - n) \beta_n [L]^n = 0 \quad (10)$$

where N is the maximum ligand number, \bar{n} the average ligand number which gives the mean number of ligands bound to one metal atom. \bar{n} can be calculated according to the equation,

$$\bar{n} = \frac{C_{HmL} - \alpha_{L(H)} [L]}{C_M} \quad (11)$$

in which $\alpha_{L(H)}$ is defined as

$$\alpha_{L(H)} = 1 + a_{H^+} K_1 + a_{H^+}^2 K_1 K_2 + \dots + a_{H^+}^m K_1 K_2 K_3 \dots K_m \quad (12)$$

where C_{HmL} is the concentration of fully protonated complexant present initially corrected at each point on the titration curve for the volume change caused by the addition of standard alkali, C_M the total metal ion concentration originally present in the titrant solution corrected for the added volume titrant and K_1, K_2, \dots, K_m are the protonation constants of the ligand. $[L]$ is the concentration of free chelating species and it can be calculated from

$$[L] = \frac{mC_{HmL} - C_{NaOH}}{a_{H^+} K_1 + 2a_{H^+}^2 K_1 K_2 \dots + ma_{H^+}^m K_1 K_2 \dots K_m} \quad (13)$$

where m is number of the protons that can be lost on forming the metal complex, and n has the same connotation as



and

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \quad (15)$$

where $[M]$ is the metal concentration and β_n the stability constant.

The details of the computer programs for calculating both ionisation and stability constants are available on request⁹.

The values of ionisation and stability constants at different temperatures and ionic strengths are reported in Tables 1 and 2. The calculated values

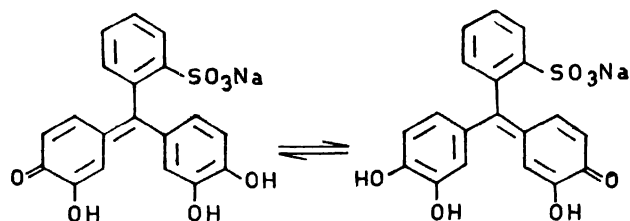
TABLE 1—VALUES OF pK_1, pK_2, pK_3 and pK_4 FOR PCV AT VARIOUS TEMPERATURES IN AQUEOUS MEDIUM

	pK_1	pK_2	pK_3	pK_4
at 25°				
0.000	6.198	8.493	8.878	10.967
0.040	6.247	8.619	8.963	11.047
0.070	6.275	8.688	9.027	11.120
0.110	6.313	8.852	9.117	11.185
0.150	6.367	8.927	9.186	11.269
at 30°				
0.000	6.158	8.458	8.781	10.858
0.040	6.207	8.579	8.876	10.929
0.070	6.234	8.649	8.942	11.002
0.110	6.272	8.802	9.049	11.050
0.150	6.325	8.877	9.120	11.135
at 35°				
0.000	6.096	8.418	8.600	10.651
0.040	6.167	8.536	8.718	10.751
0.070	6.193	8.610	8.785	10.826
0.110	6.275	8.757	8.938	10.929
0.150	6.327	8.832	9.009	11.014
at 40°				
0.000	6.067	8.396	8.595	10.606
0.040	6.126	8.499	8.669	10.661
0.070	6.154	8.571	8.735	10.736
0.110	6.212	8.691	8.801	10.752
0.150	6.265	8.765	8.873	10.838
at 45°				
0.000	6.028	8.364	8.546	10.522
0.040	6.087	8.459	8.604	10.568
0.070	6.115	8.532	8.671	10.643
0.110	6.172	8.636	8.706	10.640
0.150	6.225	8.711	8.778	10.726

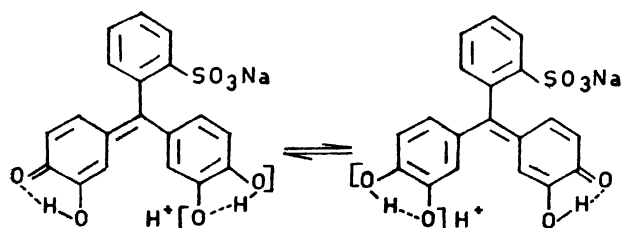
TABLE 2—VALUES OF STABILITY CONSTANTS OF PCV WITH Cu, Ni AND Zn AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

I	Stability constant $p\beta$				
	25°	30°	35°	40°	45°
With Cu					
0.000	10.921	10.795	10.576	10.544	10.454
0.040	10.889	10.767	10.576	10.478	10.372
0.070	10.885	10.750	10.573	10.463	10.334
0.110	10.858	10.738	10.574	10.379	10.253
0.150	10.825	10.697	10.573	10.338	10.179
With Ni					
0.000	8.482	8.624	8.733	8.899	8.888
0.040	8.503	8.650	8.754	8.927	8.923
0.070	8.515	8.649	8.773	8.945	9.043
0.110	8.507	8.648	8.795	8.919	9.089
0.150	8.554	8.697	8.812	8.997	9.108
With Zn					
0.000	6.945	7.147	7.244	7.411	7.599
0.040	7.090	7.225	7.288	7.461	7.619
0.070	7.107	7.242	7.305	7.478	7.649
0.110	7.233	7.374	7.370	7.549	7.659
0.150	7.371	7.392	7.388	7.573	7.685

showed ionic strength dependence and hence the thermodynamic ionisation and stability constants (pK and $p\beta$ at $I=0$) can be derived from plots of pK or $p\beta$ against I through the computer program. Inspection of the data (Table 1) shows that the values of pK_2 and pK_3 are in the same range; the identical value is due to the effect of isomerism as follows:



The intra-molecular hydrogen bonding is formed between two previous isomers as follows:



It is obvious that there are two intra-molecular hydrogen bonding: (i) formation of hydrogen bonding between two hydroxyl groups, this hydrogen bond will affect on the ionisation of the two phenolic groups resulting in pK_1 with low value and pK_2 with the highest one and (ii) formation of hydrogen bonding between hydroxyl group and quinolic group, having an effect on pK_3 and pK_4 .

The stability constants, $p\beta$, of the metal ion complexes of Cu, Zn and Ni with PCV are presented in Table 2, and the data reveal the following (i) The stability constants for different metals are decreased in the order: Cu > Ni > Zn, which is in conformity with the Irving-William order¹⁰. The stabilities of the Cu-complexes are usually higher than what could be expected from ionic radius or electronegativity considerations. This additional stability of the Cu-complexes may be attributed to the unique electronic configuration (d^9) of Cu ion which is capable of additional stabilisation due to Jahn-Teller distortion. (ii) In case of the complexation of Ni with PCV, there are two stability constants, $p\beta_1$ and $p\beta_2$. It is generally observed that $p\beta_1 \gg p\beta_2$, therefore, only $p\beta_1$ is considered in our discussion, and termed as $p\beta$ (iii) For the Cu-complex, the thermodynamic stability constants decrease as the temperature increased. However, for the Ni and Zn complexes, the thermodynamic stability constants increased as the temperature increased. Thermodynamic parameters, ΔH° , ΔG°

and ΔS° were calculated. In order to evaluate ΔH° we have fitted the equation¹¹,

$$\Delta G^\circ = RT \ln \beta = A + BT + CT^2$$

to the ionisation or stability constant values and computed the optimum value of A , B and C by the least-squares method¹²,

$$\Delta H^\circ = A - CT^2 \text{ and } \Delta S^\circ = -B - 2CT \quad (16)$$

where A , B and C are constants. Thermodynamic parameters are presented in Tables 3 and 4.

TABLE 3—THERMODYNAMIC PARAMETERS FOR IONISATION PROCESSES OF PCV AT VARIOUS TEMPERATURES

Ionisation constant	Temp. °C	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	$-\Delta S^\circ$ JK mol ⁻¹
pK_1	25	35.357	18.210	57.511
	30	35.656	16.913	61.826
	35	35.976	15.594	66.140
	40	36.317	14.254	70.454
	45	36.680	12.892	74.768
pK_2	25	48.430	13.296	117.840
	30	49.027	12.454	120.640
	35	49.636	11.598	123.440
	40	50.261	10.729	126.240
	45	50.899	9.945	129.040
pK_3	25	50.689	56.324	+ 18.899
	30	50.701	43.516	23.700
	35	50.926	30.495	66.330
	40	51.563	17.262	108.900
	45	52.015	3.815	151.500
pK_4	25	62.610	60.287	7.791
	30	62.728	50.812	39.306
	35	63.603	41.180	70.820
	40	63.436	31.190	102.334
	45	64.026	21.442	133.848

TABLE 4—THERMODYNAMIC PARAMETERS FOR COMPLEXATION OF Cu, Zn AND Ni WITH PCV AT VARIOUS TEMPERATURES

PCV	Temp. °C	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° JK mol ⁻¹
With Cu	25	62.250	-70.204	-26.677
	30	62.239	-55.431	22.459
	35	62.474	-40.412	71.595
	40	62.955	-25.148	120.732
	45	63.682	-9.638	169.868
With Zn	25	39.694	48.950	297.314
	30	41.215	53.021	310.857
	35	42.803	57.161	324.400
	40	44.459	61.368	337.943
	45	46.182	65.643	351.486
With Ni	25	48.306	62.290	370.940
	30	50.065	50.805	332.740
	35	51.633	39.129	294.540
	40	53.010	27.262	256.340
	45	54.197	15.205	218.140

For ionisation of PCV, ΔH° have positive values, indicating that these processes are endothermic. However, ΔS° have negative values, which means that the process proceeded in the deionisation direction, i.e. more ordered direction. This again is in harmony with the positivity of ΔG° .

For the Cu-complex, ΔH° has negative values indicating that these processes are exothermic. The

exothermicity decreases as the temperature increases. Entropy changes (ΔS°) have negative values at 25°, then it changes to positive values in the range 30–45°, i.e. as the temperature increases the process proceeds in the complexation direction. For the Zn and Ni complexes, ΔH° has positive values which indicates that these processes are endothermic. The endothermicity increases by temperature for Zn and decreases for Ni. All ΔS° values for the Zn and Ni complexes are positive. This is in good agreement with the negative values of ΔG° .

In addition to the solvation effects, there appears to be a natural tendency for ΔH° and ΔS° terms to contain contributions of the same sign. Attractive forces impose constraint (ΔH° and ΔS° both negative), and the release of such forces confers greater freedom (ΔH° and ΔS° both positive, for the Ni- and Zn-complexes). This is often referred to as the normal compensation. But in case of the Cu-complexes, this fact is not completely true.

If, on the other hand, we apply a new approach¹⁸, namely, linear free energy relationship (LFER), then, equation (1) can be simplified as

$$\Delta G_{ML}^\circ = B \Delta G_{MsL}^\circ + R \quad (17)$$

where R is a constant. The plot of ΔG_{ML}° against ΔG_{MsL}° is linear in nature with slope B (Fig. 1).

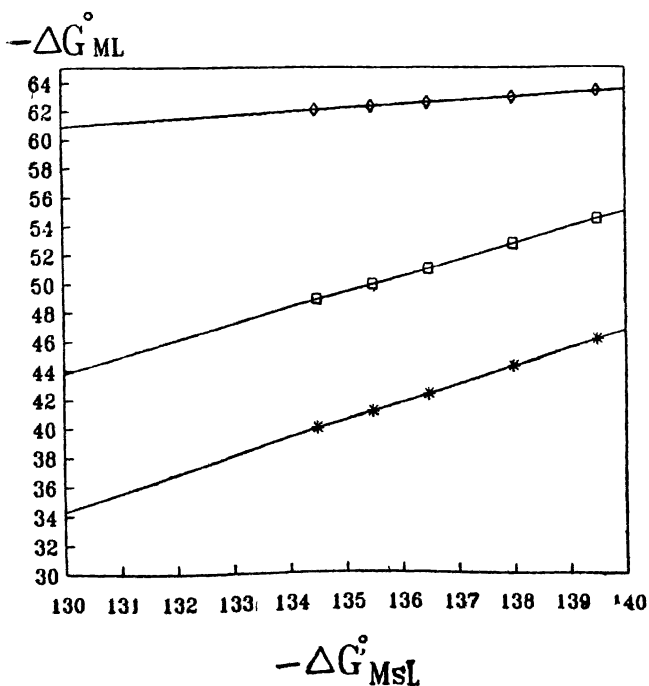


Fig. 1. Plots of ΔG_{ML}° vs ΔG_{MsL}° at different temperatures : (\diamond) Cu, (\square) Ni and ($*$) Zn.

Slope B is invariant within the range of $\log K$ values encompassed. B must depend on properties

or variables ascribable to both the change in temperature and the change in metal ion from Ms to M. Accordingly, two standard reaction series were postulated: the one dependent only on changes in the temperature, and the other dependent only on changes in the metal ion. This dependence was represented by an exact differential in which B appeared as partial differential gradient. The values of B are 1.254, 1.126 and 0.259 for the Zn, Ni and Cu-PCV complexes respectively. Inspection of the values of B for the complexes of PCV reveals that B has positive values which indicates that the change of stability standard free energy is directly proportional to protonation standard free energy. B values decrease in the following order: Zn > Ni > Cu, which means that the change of free energy for the Cu-complex is the lowest in comparison with the other two complexes.

Experimental

Pyrocatechol violet (PCV) (Sigma) was used. Carbonate-free NaOH (B.D.H.) solution, used as titrant, was prepared according to the standard method¹⁴. NaClO_4 (A.R.) was used to fix the ionic strength of the measured solutions. Deionised distilled water was used for preparing all solutions.

Potentiometric pH-titrations were carried out using a G 104 pH-meter radiometer (calibrated with both phthalate buffer at pH 4 and borax buffer at pH 9.18)¹⁵.

All measurements were carried out at 25, 30, 35, 40 and 45° in aqueous medium at ionic strengths of 0.04, 0.07, 0.11 and 0.15 using NaClO_4 as the fixer.

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