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Conductometric and Spectrophotometric Studies on Copper(II), Zinc(II) and Cadmium(II) Complexes of 4-(2-pyridylazo) Resorcinol

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The reaction between copper(II), Zinc(II) and cadmium(II) and 4-(2-pyridylazo) resorcinol leads to the formation of complexes having the formula $M_nX_mL_y$ [M = Cu(II), Zn(II) or Cd(II); n = 1 or 2, X = Cl, m = 0, 1; L = 4-(2-pyridylazo) resorcinol (PAR), y = 0.5, 1 or 2]. The complex formation was studied by conductometric titrations and conductometric measurements and spectrophotometrically at pH 2.15–11.25. The Cu(II)-Zn(II)- and Cd(II)-PAR complexes absorb at $\lambda = 500$ (pH = 9.81), 495 (pH = 8.12) and 480 nm (pH = 8.75) respectively. Stoichiometry (2 : 1, 1 : 1, 1 : 2), formation stability constants and thermodynamic parameters (Δ°G, ΔH and ΔS) have been evaluated and the values of which are in the order Cd- > Zn- > Cu-PAR complexes. The reagent is made use of for the determination of 0.63 ppm Cu, 0.32 ppm Zn and 0.42 ppm Cd.

INTRODUCTION

4-(2-Pyridylazo) resorcinol (PAR) was used as a complexometric indicator and for the spectrophotometric determination of Sc, In, U and Nb[1] and V[2]. The present paper reports the conductometric titrations and conductometric measurements and the spectrophotometric studies of Cu(II)-, Zn(II)- and Cd(II)-4-(2-pyridylazo) resorcinol complexes.

EXPERIMENTAL

All chemicals used were of AnalaR grade (99.9%, BDH, E. Merck or Sigma). 1×10^{-4}M-Cu(II), Zn(II) and Cd(II), 1×10^{-3}M-4-(2-pyridylazo) resorcinol solutions were prepared by dissolving the appropriate amounts of $CuCl_2$, $ZnCl_2$ and $CdCl_2$, and 4-(2-pyridylazo) resorcinol in double distilled water[3]. Buffer solutions of pH 2.15–11.25 were prepared following standard methods[4]. Pye Unicam Model 290 MK2 pH Meter was used for buffer solutions standardisation.

Conductometric titrations were carried out by titrating specific volumes (V_1) of 1×10^{-4}M aqueous solutions of the metal ions with aliquots (0.5 ml increments) of 1×10^{-3}M-4-(2-pyridylazo) resorcinol (V_2) and the conductances measured after stirring the solutions magnetically for 5 min at 25°C. The specific conductances were corrected for dilution: $(\lambda \times V_1 + V_2/V_1)$. Conductometric measurements were carried out using a constant concentration of the metal ions and variable concentrations of 4-(2-pyridylazo) resorcinol, keeping the total volume constant and thermostating the solutions at 30°C for 2 hrs. Molar conductivities of the solutions were measured using a CM 25 conductivity meter, made by WPA Saffron Walden, England.

The spectrophotometric measurements in the ultraviolet-visible 190–700 nm region were performed using a Shimadzu spectrophotometer model UV-240. The M(II)-PAR solutions were prepared by mixing the metal ions with the ligand-buffer mixture using a blank containing the same ligand concentrations as in the test solutions to compensate absorbance due to ligand.

RESULTS AND DISCUSSION

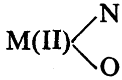
Conductivity Experiments

The results of the conductometric titrations and measurements reveal the formation of 2 : 1, 1 : 1 and 1 : 2 (M : L) complexes. The conductance values increase with the increase of ligand concentration as a result of the increase of the diffusion coefficient of the diffusion particles. Increase of conductance may be ascribed to the liberation of hydrogen ions having faster movements and high mobility and increase the conductance power of the solutions[5].

Spectrophotometric Measurements

In order to investigate the factors affecting the complex formations, the spectral absorbance of the complexes, effect of pH, effect of ligand concentration, effect of metal ion concentration and validity of Beer's law were studied.

Effect of pH

For studying this factor, constant concentrations of metal ion (5×10^{-5} M) and ligand (2×10^{-4} M) were prepared in buffer solutions of pH 2.15–11.25. The spectral absorbances of these solutions increase with the increase of pH until they reach maxima at pH 9.81 [Cu(II)-PAR, $\lambda_{max} = 500$ nm], 8.12 [Zn(II)-PAR, $\lambda_{max} = 495$ nm] and 8.75 [Cd(II)-PAR, $\lambda_{max} = 480$ nm], thereafter, they decrease. These spectral changes with pH may be due to progressive and continuous formation of different convertible species of complexes. The increase of absorbance with pH may be due to the increased tendency for the formation and maximum development of complexes having extrastabilities, whereas the decrease of absorbance is due to dissociation to complexes of lower stoichiometry, or the formation of hydroxo complexes. The bands (220, 240, 390, 410, 470 nm) of the ligand at different pH values shift due to nonconjugation of the heterocyclic pyridine, N=N and resorcinol [Cu(II)-PAR-230, 270, 315, 500, 530 nm; Zn(II)-PAR, 220, 265, 315, 495, 500, 530 nm; Cd(II)-PAR, 225, 260, 320, 370, 480, 500, 530 nm] and on complexation they shift to shorter wavelengths. This lower shift (hypsochromic shift) may be due to a shift in ionisation ($HL \rightarrow L^- + H^+$) and the increased single electron delocalisation of nonbonding orbitals of the nitrogen atom and OH group which denotes that the $n - \pi$ and $\pi - \pi^*$ transitions are influenced by intra and intermolecular charge transfer, whereas the shift to longer wavelength (bathochromic shift) may be due to excited transition ($\pi - \pi^*$, charge transfer) of the pyridine ring and resorcional and d–d transition (ν Cu(II)-PAR = 20000 cm^{-1}, ν Zn(II)-PAR = 20202 cm^{-1}, νCd(II)-PAR = 20833 cm^{-1}). The formed complexes absorb lesser amounts of energy than those appearing at shorter wavelengths (absorbing large amounts of energy) in solution. Present electronic spectral studies in visible region (λ_{max} Cu(II)-PAR = 500 nm, λ_{max} Zn(II)-PAR = 495 nm, λ_{max} Cd(II)-PAR = 480 nm) are consistent with the data for tetragonally distorted octahedral complexes. The electronic spectra in the pH 2.15–9.81, 2.15–8.12 and 2.15–8.75 for Cu(II)-, Zn(II)- and Cd(II)-PAR, respectively, range show a slight intensification of absorption band with increase of pH. This increase in band intensity may be attributed to the lowering of symmetry (distortion of octahedral geometry) which, in turn, may be attributed to the deprotonated phenolic linkage, resulting in short  bonds. Thus, shift may be due to a coupling of $n - \pi$, $\pi - \pi^*$, C.T. and d–d transitions. These shifts could be accounted for by an easier excitation of the single electron of the pyridine, N = N and resorcinol structures which, in turn, can be ascribed to a higher delocalization of the electron clouds on the rings. The bands of longest wavelength can be assigned to an inter, intramolecular charge transfer and d–d transitions. 4-(2-Pyridylazo) resorcinol is known to act as a bidentate ligand in chelation reaction with metal ions. Metal ions (Cu, Zn, Cd) may either accept π-bonding to be mixed with their vacant orbitals of donor atoms (N, O). The π electron density around the donor atom influences the metal-ligand bonds. The metal ions (Cu, Zn, Cd) exhibit a strong complexing tendency due to their small size and availability of orbitals for coordinate and covalent bond formation. However, the presence of excess ligand in this study results in suppressing the hydrolysis of Cu(II), Zn(II) and Cd(II) ions and thus more coordinate sites would be available for complexation.

Effect of Ligand Concentration

Keeping the metal ion concentration constant (2×10^{-4} M), the ligand concentrations were varied in the range $1\text{–}8 \times 10^{-5}$ M. The absorbances increase gradually with the increase of [ligand] reaching more or less constant absorbances when sufficient excess of 4-(2-pyridylazo) resorcinol has been added. Increase of absorbance may be attributed to gradual complex formation having large [PAR], then reach a limiting value. As [PAR] increases λ_{max} does not change. This may be ascribed that the complexes of the same metal having different composition (stoichiometry), absorb at the same wavelength (d–d transition).

Effect of Metal Ion Concentration

The concentration of ligand (1×10^{-4} M) is kept constant while that of Cu(II), Zn(II) or Cd(II) is varied (2×10^{-5} M – 1×10^{-4} M). The absorbances of the solutions increase apparently with the increase of metal ion concentrations. This may be attributed to the probable and continuous tendency for enhancing the metal ions and ligand characters towards the formation of complexes having large concentration of ligand (high stoichiometric ratios).

Validity of Beer's Law

Beer's law is valid for introducing 4-(2-pyridylazo) resorcinol as an analytical complexing reagent for the microdetermination of 0.63–6.50 ppm Cu($\epsilon = 4.6 \times 10^5$ cm^2. mol^{-1}), 0.32–4.00 ppm Zn($\epsilon = 3.4 \times 10^6$ cm^2· mol^{-1}) and 0.42–7.25 ppm Cd($\epsilon = 4.3 \times 10^6$ cm^2·mol^{-1}).

Stoichiometry of the Complexes

The stoichiometric composition of Cu(II)-, Zn(II)- and Cd(II)-PAR complexes were determined by conductometric studies and spectrophotometric methods (molar ratio, M.R.[6]; continuous variation, C.V[7–9]; straight line, S.L.[10,11]; slope ratio, S.R.[12]; and limiting logarithmic, L.L.[13]). The results reveal the formation of 2 : 1, 1 : 1 and 1 : 2 (M : L) ratios.

The apparent conditional stability constant and thermodynamic parameters

The apparent conditional formation constant (K_f). free energy changes ($\Delta°G$), enthalpy (ΔH) and entropy (ΔS) of Cu(II)-, Zn(II)- and Cd(II)-PAR complexes are evaluated making use of the results of spectrophtometric methods[6–13]

$$K_f = \frac{A/A_m}{(1 - A/A_m)^{n+1} \cdot n^2[L]^2}$$

$K_f = 1/kc^{-1}/kd$, $\beta_n = \log (A/\epsilon_n) - m \log [M^{n+}] + n \log [L]$ and the analytical ($pH = \log (A/A_L - A) + pK_f + n\ pKi - n \log [H^+]$) methods[14]. The free energy changes of the complexes can be evaluated using the equation : $\Delta°G = -RT \ln k$. Enthalpy (heat content, ΔH) and entropy (ΔS) can be estimated using the relations :

$\Delta H = 2T_1T_2 \ln k/(T_2 - T_1)$, $\Delta S = (\Delta H - \Delta°G)/T_1$ where (R = gas constant, $T_1 = 25 + 273$ k° and $T_2 = 30 + 273$ k°, K_f = formation stability constant. K = dissociation constant of the complex.

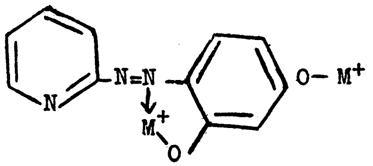
Stoichiometry, formation constants, free energy changes, enthalpy and entropy values of the complexes are recorded in Table 1. The values

TABLE 1

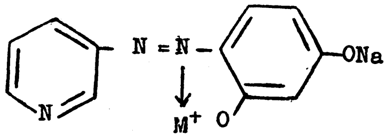
STOICHIOMETRY, CONDITIONAL FORMATION CONSTANT, FREE ENERGY CHANGES (AT 25°C), ENTHALPY AND ENTROPY (25–30°C) DATA OF Cu(II)-, Zn(II)- AND Cd(II)-4-(2-PYRIDYLAZO) RESORCINOL COMPLEXES

Method	Ratio	K_f	$\Delta°G$ Kcal. mol^{-1} deg^{-1}	ΔH Kcal. mol^{-1} deg^{-1}	ΔS Kcal. mol^{-1} deg^{-1}
			Cu(II)-PAR complexes		
M.R.	1 : 2	6.891×10^{12}	17.622	1067.873	3.524
C.V.	2 : 1	3.840×10^{10}	14.528	880.392	2.906
	1 : 1	1.188×10^{12}	16.574	1004.369	3.315
	1 : 2	2.647×10^{12}	17.051	1033.310	3.410
S.L.	1 : 1	3.565×10^{8}	11.738	711.340	2.348
	1 : 2	1.663×10^{8}	11.284	683.804	2.257
L.L.	1 : 1	1.100×10^{6}	8.292	502.516	1.659
S.R.	1 : 1				
	1 : 2				
pH	1 : 1	2.144×10^{9}	12.808	776.160	2.562
			Zn(II)-PAR complexes		
M.R.	1 : 1	7.7×10^{12}	17.688	1071.883	3.538
	1 : 2	6.376×10^{14}	20.321	1231.425	4.064
C.V.	2 : 1	6.593×10^{10}	14-850	899.919	2.970
	1 : 1	8.524×10^{11}	16.376	992.377	3.275
S.L.	1 : 1	2.270×10^{12}	16.960	1027.760	3.392
	1 : 2	2.072×10^{15}	21.023	1273.999	4.206
L.L.	1 : 1	1.413×10^{7}	9.814	594.740	1.963
S.R.	1 : 1				
	1 : 2				
pH	1 : 1	1.424×10^{6}	8.446	511.842	1.689
			Cd(II)-PAR complexes		
M.R.	1 : 1	2.843×10^{12}	17.094	1035.891	3.419
	1 : 2	8.762×10^{13}	19.137	1159.729	3.827
C.V.	2 : 1	7.568×10^{10}	14.932	904.901	2.986
	1 : 1	7.856×10^{12}	17.670	1071.344	3.536
	1 : 2	7.923×10^{14}	20.450	1239.272	4.09
S.L.	2 : 1	3.425×10^{10}	14.46	876.261	2.892
	1 : 1	5.728×10^{12}	17.517	1061.535	3.503
	1 : 2	4.345×10^{15}	21.4366	1300.75	4.293
L.L.	1 : 1	9.732×10^{10}	15.0823	913.986	3.017
	1 : 2	6.795×10^{14}	20.3585	1233.724	4.0717
S.R.	1 : 1				
	1 : 2				
pH	1 : 1	4.624×10^{8}	11.8935	720.746	2.3787

obtained indicate that the 1 : 2 complexes are the most stable. The order of stability constants (K_f), activation energy changes ($\Delta°G$), enthalpy (ΔH) and entropy (ΔS) are Cd(II)- > Zn(II)- > Cu(II)-PAR complexes. Values of enthalpy (heat content, ΔH), and entropy (ΔS) of activation are found to be negative and high and increase on going from M_2L to ML_2 complexes. This may be due to a change in dentate character of the ligand as a result increasing the coordination number of the metal ion. Negative values of enthalpy and entropy indicate that the reaction between the ligand and the metal ions is endothermic and the reactant molecules suffer from a loss of some internal degrees of freedom during the process of formation of complexes. The change in the negative values of enthalpy and entropy may be related to the decrease in randomness and indicate that the activated complexes are more ordered. The coordination between the ligand and the metal ions takes place through coordinate bond between the metal ion and the nitrogen atom and covalent bond between the metal ion and the oxygen atom of the OH phenolic group of resorcinol. Linkage between 4-(2-pyridylazo) resorcional and the metal ions are presented as follows :



2 : 1 M(II)-PAR complex



(1 : 1) M(II)-PAR complex

REFERENCES

1. A. I. Busev, V. G. Tiptsova and V. M. Ivanov, Analytical Chemistry of Rare Elements, Mir Publishers, Moscow (1981).
2. F. B. Martiner and A. L. Pena, *Acta Cient. Composlelana*, **8**, 209 (1971).
3. A. I. Vogel, Text-book of Quantitative Inorganic Analysis including Elementary Instrumental Analysis, 4th ed., The English Book Society and Longaman (1982).
4. H. T. S. Britton, Hydrogen Ions, 4th ed. (1956).
5. I. M. Issa, R. M. Issa and R. M. Awadallah, *Egypt J. Chem.*, **18**, 221 (1975).
6. Yoe and Jones, *Ind. Eng. Chem. Anal. Ed.*, **16**, 111 (1944).
7. P. Job, *Comp. Rend. (Paris)*, **180**, 928 (1925); *Ann. Chim. (Paris)*, **9**, 133 (1928).
8. W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

9. F. G. Scherief and A. M. Awad, *J. Inorg. Nucl. Chem.*, **24**, 149 (1962).
10. E. I. Asmus, *Z. Anal. Chem.*, **178**, 104 (1960).
11. Korkuc, A. Sommer and T. Lipiec, Theory and Structure of Compounds, (Ed.) Trzebia-Towaka, Pergamon Press (1962).
12. A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).
13. H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941).
14. R. M. Awadallah, M.Sc. Thesis. Assiut Univ., Egypt (1971).

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