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Note

Complexation of *o*-Vanillin with Some First Transition Cations in Aqueous Ethanol (70%) Medium

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The present paper summarizes the complexation behaviour of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 2-hydroxy-3-methoxybenzaldehyde examined by Crow's mean diffusion coefficient method. Diffusion currents of polarographic waves were used to determine the stability constants of the 1 : 1 and 1 : 2 complexes of the respective ions (298 K) which were 4.0, 2.7; 4.7, 3.3; 5.4, 2.5; 5.3, 3.5 and 4.5, 3.5, respectively. Overall stability constants at three temperatures 288, 298 and 308 K yielded the thermodynamic parameters.

INTRODUCTION

Complexation with bidentate ligands like salicylaldehyde[1] has been of special interest because of their potential applicability for analytical purposes. Goel reported stepwise complex-formation of *o*-vanillin with some first transition metal cations using the potentiometric titration method.[2] The present work was a part of a program of examining the utility of Crow's mean diffusion coefficient method[3–5] as applied to diffusion currents of the quasi-reversible and irreversible polarographic waves of single and mixed ligand complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with some bidentate ligands. In this communication we report the results of our polarographic studies of the complexes of these cations with 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) at 288, 298 and 308 K. The values of stability constants and of ΔG, ΔH and ΔS are given.

EXPERIMENTAL

Metal perchlorates used in this work were prepared from reagent grade oxides, hydroxides or carbonates of metals by dissolving them in perchloric acid (AR) and crystallizing the salts twice from double-distilled water. Reagent grade *o*-vanillin was obtained from Ega Chemie, West Germany and the gelatin was of analytical grade. Commercial ethanol was made aldehyde-free by the usual methods and then distilled. IOLAR grade nitrogen gas (Indian Oxygen Ltd.) was used for deareation of solutions.

The test solution contained the metal ion (1.0 mmol dm^{-3}), $LiClO_4$ (0.1 mol dm^{-3}) gelatin (0.005%), *o*-vanillin (varying from 0.01 mmol to 5.0 mmol dm^{-3}) and ethanol (50 volume percent in water). The pH's of the solutions were adjusted to specified values (given below) by LiOH or $HClO_4$ solutions before making up the final solutions.

The apparatus used were ELICO LI-120 digital pH-meter, Polariter PO4g Radiometer polarograph (run at a chart speed of 2 cm min^{-1}), Julabo F40 (West

Germany) circulating thermostat and Sargent capillary $m = 1.68$ mg s^{-1} and $t = 4.3$ s for 70 cm Hg head in aqueous $LiClO_4$ solution (0.1 mol dm^{-3}) at zero potential (SCE). The double-walled Kalousek cell was used for the investigation.

TABLE I

M(II)-o-vanillin (ethanol-water 70% v/v) system

$M(ClO_4)_2$ 1.0 mmol dm^{-3} Temperature 298 K
$LiClO_4$ 0.1 mol dm^{-3} pH's 6.4, 7.6, 6.8, 4.2 and 8.5 respectively from left to right

[L]	$-E_{1/2}$(Mn)	$\bar{i}_d$(Mn)	$-E_{1/2}$(Co)	$\bar{i}_d$(Co)	$-E_{1/2}$(Ni)	$\bar{i}_d$(Ni)	$-E_{1/2}$(Cu)	$\bar{i}_d$(Cu)	$-E_{1/2}$(Zn)	$\bar{i}_d$(Zn)
mol dm^{-3}	V	μA	V	μA	V	μA	V	μA	V	μA
0.00000	1.34	3.25	1.32	1.11	1.10	1.60	0.12	3.84	1.20	2.67
0.00001	1.36	3.21	1.33	1.03	1.13	1.34	0.14	3.66	1.23	2.59
0.00005	1.37	3.18	1.34	1.01	1.15	1.30	0.16	3.64	1.24	2.57
0.00010	1.39	3.16	1.36	0.99	1.18	1.28	0.18	3.60	1.26	2.55
0.00050	1.41	3.11	1.38	0.95	1.20	1.26	0.20	3.57	1.29	2.51
0.0010	1.42	3.10	1.40	0.93	1.22	1.24	0.21	3.54	1.31	2.47
0.0020	1.44	3.09	1.41	0.92	1.24	1.20	0.22	3.46	1.32	2.45
0.0050	1.45	3.01	1.43	0.88	1.25	1.18	0.24	3.32	1.34	2.41

$\log \beta_2$ (Mn) = 6.7; $\log \beta_2$ (Co) = 8.0; $\log \beta_2$ (Ni) = 7.9;
$\log \beta_2$ (Cu) = 8.8; $\log \beta_2$ (Zn) = 8.0

RESULTS AND DISCUSSION

Polarograms were recorded for test solutions containing Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) and o-vanillin (0 to 5.0 mmol dm^{-3}) at apparent pH values of 6.4, 7.6, 6.8, 4.2 and 8.5, respectively, which values were chosen from the titration curves of Goel.[2] A well-defined single diffusion-controlled wave was obtained in each case which gave a linear semi-log plot with reciprocal slope lying between 40 and 50 mV per decade. The half wave potentials for each metal ion shifted to negative values and the diffusion current decreased with increasing concentration of ligand. Decreases in diffusion currents ($\Delta \bar{i}_d$) were plotted against the log ligand concentration and the area under the curve at each ligand concentration yielded $\log F_o'$ [L] values. These values were then plotted against log [L] and the limiting slope of the curve yielded (N_{max}/k) values. From the knowledge of the maximum coordination number N_{max} for the metal ion, the k values were calculated. Multiplying $\log F_o'$ [L] values by k values yielded $\log F_o$ [L] values. The F_j [L] *vs.* [L] plots then gave the values of formation constants.[3,6,7]

TABLE II

Overall stability constants and thermodynamic parameters of bivalent metal complexes with o-vanillin

Metal ion	$\frac{T}{K}$	$\log \beta_2$	$\frac{-\Delta G}{kJ\ mol^{-1}}$	$\frac{-\Delta H}{kJ\ mol^{-1}}$	$\frac{\Delta S}{JK^{-1}\ mol^{-1}}$
Mn(II)	288	7.01—7.05	38.76		
	298	6.60—6.75	38.66	50.7	—40.5
	308	6.45—6.55	37.85		
Co(II)	288	8.23—8.25	47.15		
	298	8.02—8.06	45.91	62.2	—54.8
	308	7.78—7.80	44.81		
Ni(II)	288	7.97—8.03	44.51		
	298	7.92—7.94	44.06	45.8	—5.2
	308	7.50—7.60	43.70		
Cu(II)	288	9.10—9.16	50.35		
	298	8.73—8.81	48.46	81.7	—111.6
	308	8.14—8.20	46.79		
Zn(II)	288	8.08—8.10	44.67		
	298	7.99—8.01	45.47	51.2	—19.1
	308	7.96—8.02	47.06		

The polarographic studies were carried out at three temperatures 288, 298 and 308 K for the present metal-ligand systems and the results for 298 K are given in Table I. The overall stability constant values ($\log \beta_2$) for the series of complexes, given in ranges, are tabulated in Table II. This table also shows that the order of overall stability constants approximately obeys Irving and Williams[8] and Mellor and Maley[9] natural order, which is $Mn < Co \approx Ni < Cu > Zn$ in this case. The ΔG, ΔH and ΔS values of the complexes are also given in Table II which shows that the free energies and enthalpies of formation have large negative values in each case, indicating spontaneity of complex formation. The negative entropy values for some of the complexes indicate higher orders in these complex molecules.

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SAŽETAK

Stvaranje kompleksa nekih kationa prijelaznih metala sa *o*-vanilinom u miješanom otapalu etanol/voda

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U ovom radu prikazani su rezultati polarografskih istraživanja stabilnosti kompleksa Mn(II), Co(II), Ni(II), Cu(II) i Zn(II) iona sa 2-hidroksi-3-metoksibenzaldehidom Crowovom metodom srednjih difuzijskih koeficijenata. Na temelju difuzijskih struja polarogarfskih valova određene su konstante stabilnosti kojih logaritmi iznose 4,0 i 2,7 za Mn(II), 4,7 i 3,3 za Co(II), 5,4 i 2,5 za Ni(II), 5,3 i 3,5 za Cu(II) i 4,5 i 3,5 za Zn(II) komplekse tipa 1 : 1 i 1 : 2. Termodinamički parametri određeni su na temelju temperaturne ovisnosti (288, 298 i 308 K) kumulativnih konstanti stabilnosti.