Polarographic Study of Cd(II)-Acetylacetonate System

(Km.) KRISHNA, S. K. JHA and MUKHTAR SINGH

Chemical Laboratories, Agra College, Agra

Manuscript received 7 April 1979, revised 4 February 1980, accepted 18 March 1980

BRANICA[1,2] and co-workers have undertaken polarographic investigations on acetylacetonate complexes of Cu(II) and Ni(II). The present study deals with the polarography of Cd(II)-acetylacetonate system.

Experimental

Solutions of $CdCl_2$, $NaNO_3$ were prepared from reagent grade chemicals in conductivity water. Acetylacetone was of E. Merck G. R. grade and its aqueous solution was used as ligand. The concentration of Cd(II) in each case was kept at 1×10^{-3} *M*. The concentration of acetylacetonate ion was calculated from the *p*H of the solution and pK value[3-5] of acetylacetone (pK=8.95).

A manual polarograph (Toshniwal CLO2) with polyflex galvanometer (Toshniwal PL-50) was used. All the measurements were recorded at 30 ± 0.1°. Purifleed nitrogen gas was passed through the solution to remove the dissolved oxygen. Saturated calomel electrode (S. C. E.) was used as reference electrode. The d.m.e. had the following characteristics (in 0.1*M* $NaNO_3$, open circuit) : m=1.673 mg/sec, t=4.04 sec, $m^{2/3}\,t^{1/6}=1.778\ mg^{2/3}\ sec^{-1/2}$, $h_{corr}=63.01$ cm. The number of electrons(n) involved in the reduction process was determined by millicoulometric method of DeVries and Kroon[6]. This gave the value of n=2 at *p*H 7.

The thermodynamic functions (△G, △H and △S) have been evaluated using relevant equations[7].

Results and Discussion

Polarograms of the solutions containing 1×10^{-3} *M* Cd(II) and 0.1 *M* acetylacetone were taken at different *p*H values. It was observed that the negative shift in $E_{1/2}$ was maximum at *p*H 7 and hence this value was chosen for studying the complex formation between Cd(II) and acetylacetone. The concentration of the ligand was varied from 0.01 to 0.1 *M*. In each case a single well-defined wave appeared. The plots of i_d vs $h^{1/2}_{corr}$ were found to be linear and passing through the origin thereby indicating that the reduction is diffusion-controlled. The plots of log $i/i_d - i$ vs $E_{d.e.}$ were found to be linear with slope of the order of 31 ± 2 mV. This shows that the reduction is reversible. The plot of $E_{1/2}$ against $-\log C_x$ is s straight line. This suggests that Cd(II) forms a single complex with the ligand. The composition and stability constants have been determined by Lingane's[8] method.

The value of co-ordination number, p, comes out to be 1. The composition of the complex is, therefore, $[Cd(Acac.)]^+$. The value of stability-constant has been determined at three different temperatures (20°, 30° and 40°).

The values of stability constant (β) and the thermodynamic functions (△G, △H and △S) have been summarised in Table 1.

TABLE 1—VALUES OF LOG β AND △G, △H AND △S AT DIFFERENT TEMPERATURES FOR Cd(II)—ACETYLACETONATE SYSTEM μ=0.1 ($NaNO_3$)

Temp. °C	log β	△H Kcal mole^{-1}	△G Kcal mole^{-1}	△S cal degree^{-1} mole^{-1}
20	4.28	−11.897	−5.74	−0.020
30	3.99	−11.897	−5.44	−0.021
40	3.69	−11.897	−5.12	−0.022

Acknowledgement

Thanks are due to the Principal, Agra College, Agra for providing necessary facilities.

References

1. M. PETEK, L. JEFTIC and M. BRANICA, "Polarography 1964", Vol. I (Proceedings IIIrd Intern. Congr. Southampton) Edited, G. J. Hills, McMillan, London, 1966, p. 491.
2. M. VERGI, B. COSVIC and M. BRANICA, *J. Electroanal. Chem.*, 1969, 3, 22.
3. G. SCHWARZENBACH and K. LUTZ, *Helv. Chim. Acta*, 1940, 23, 1147.
4. W. WALISCH and A. H. RUPPERSBERG, *Ann. Univ. Saraviensis*, 1959, 8, 1.
5. M. L. EIDINOFF, *J. Amer. Chem. Soc.*, 1945, 67, 2072.
6. T. DEVRIES and J. L. KROON, *J. Amer. Chem. Soc.*, 1953, 75, 2484.
7. T. B. TRIVEDI, M. S. PATEL and D. N. VYAS, *J. Indian Chem. Soc.*, 1977, 54, 560.
8. J. J. LINGANE, *Chem. Rev.*, 1941, 29, 1.

Chemical Investigation of Some Mangrove Species : Part VIII. *Lumnitzera racemosa*

S. GHOSH MAJUMDAR and GOURI PATRA

Department of Chemistry, The University of Burdwan, Burdwan 713 104

Manuscript received 6 August 1979, accepted 17 Mach 1980.

A thorough investigation for secondary metabolites of Sundarban mangroves have been undertaken for chemotaxonomic consideration[1-6]. In this present communication triterpenoid constituents of *Lumnitzera racemosa* (Fam. Combrataceae) from two different latitude viz. Kakinada (Lat 20°. NH) and Sundarban (Lat. 16° NH) are described to determine the effect of Insolation upon taxonomic markers.

TABLE 1

Species/Habitat	Portion in Kg.	Compound Isolated					
		A	B	C	D	E	F
L. racemosa Sunderban	Bark 1.75	0.35 g	0.25 g	0.50	0 02	1.00	0.08
	Leaves 3.0	0.50 g	0.15 g	1.50	0.25	0.08	0.10
L. racemosa Kakinada	Bark 3.0	0 70	0.30	0.35	0.05	0.75	0.09
	Leaves 3.0	0.35 g	0.20 g	0.60	0.20	0.60	0 10

A = β-amyrin, B = taraxerol, C = friedelin, D = betulin, E = β-sitosterol, F = triacontanol, g = identified through glc study.

Literature survey showed that the genus Lumnitzera remained unexplored. A species of the genus is a small tree (20-40 ft high), were collected in the month of December from two habitats.

Petroleum extract of dry, powdered bark of the plant from Sundarban was taken up in ether and separated into neutral and acidic fraction as usual procedure[1]. Each of the two fractions were then chromatographed over silica gel G, the former one directly and the latter after esterification with diazomethane. On working up of the acidic fraction it was found to contain a few complex waxy material without any trace of triterpenes.

The neutral fraction on separation over silica gel G furnished the following compounds. Similar compounds with slight variations in yield were isolated (Table 1) from the plant material of Kakinada.

The identity of the constituents was made through m. p., mixed m.p., tlc., co-tlc., glc studies and preparation of some derivatives.

(a) Friedelin m.p. 248° (oxime, m.p. 2[x]4°) $[\alpha]_D$ − 71°

(b) β-amyrin m.p. 195° (Ret. time 17.7 mins. at 250°, column material : 3% SE 30 on gas chromz 60-80 mesh).

(c) Taraxerol m.p. 268° (Ret. time 20.0 mins. at 250°).

(d) Triacontanol (m.p. 82°).

(e) Betulin m.p. 238 (acetyl, m.p. 212°).

(f) β-sitosterol m.p. 138° $(\alpha)_D$ − 35°.

Acknowledgement

We are highly indebted to Sri Prabal Sil and other laboratory colleagues for their constant encouragement and help.

References

1. S. GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1979, 56, 111.
2. S. GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1976, 53, 947.
3. S. GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1976, 53, 1241.
4. S. GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1978, 55, 414.
5. S GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1979, 56, 218.
6. S. GHOSH MAJUMDAR and GOURI PATRA, *J. Indian Chem. Soc.*, 1979, 56, 1039.