

Ag—O (nitrate) and Cd—O (nitrate) stretching modes could not be observed above 200.

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References

1. AHUJA, I. S. & RASTOGI, P., *J. chem. Soc.*, (1970), 2161, and refs. 9-13 therein.
2. AHUJA, I. S. & GARG, A., *Indian J. Chem.*, **9** (1971), 1307.
3. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1971.
4. FIELD, B. O. & HARDY, C. J., *Q. Rev. chem. Soc.*, **18** (1964), 361; ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D., *Q. Rev. chem. Soc.*, **25** (1971), 289; ADDISON, C. C. & SUTTON, D., *Prog. inorg. Chem.*, **8** (1967), 195.
5. GATEHOUSE, B. M., LIVINGSTONE, S. E. & NYHOLM, R. S., *J. chem. Soc.*, (1957), 4222.
6. CURTIS, N. F. & CURTIS, Y. M., *Inorg. Chem.*, **5** (1965), 804.
7. ADDISON, C. C. & GATEHOUSE, B. M., *J. chem. Soc.*, (1960), 613.
8. HART, F. A. & LAMING, F. P., *J. inorg. nucl. Chem.*, **27** (1965), 1605; 1825.
9. BULLOCK, J. I., *J. inorg. nucl. Chem.*, **29** (1967), 2257.
10. LEVER, A. B. P., MANTOVANI, E. & RAMASWAMY, B. S., *Can. J. Chem.*, **49** (1971), 1957. KARAYANNIS, N. M., MIKULSKI, C. M., PYTLEWSKI, L. L. & LABES, M. M., *J. inorg. nucl. Chem.*, **34** (1972), 3139; *Inorg. Chem.*, **13** (1974), 1146. SPECA, A. N., PYTLEWSKI, L. L., KARAYANNIS, N. M. & OWENS, C., *J. inorg. nucl. Chem.*, **36** (1974), 3151; AHUJA, I. S., SINGH, RAGHUVIR & SINGH, RAJINDAR, *Spectrochim. Acta*, **32A** (1976), 547.
11. ROSENTHALL, M. R. & DRAGO, R. S., *Inorg. Chem.*, **4** (1965), 840.
12. FERRARO, J. R. & WALKER, A., *J. chem. Phys.*, **42** (1965), 1273.

Polarographic Study of Zn(II)-Tryptophan System

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Polarographic behaviour of Zn(II) in the presence of DL-tryptophan and NaClO₄ as supporting electrolyte has been studied. The system yields two waves, however, the second is masked by a maximum at low tryptophan/Zn(II) ratios. The maximum disappears on increasing the [tryptophan] but at this stage the second wave is considerably suppressed and is finally eliminated on further increase of tryptophan/Zn(II) ratio. The first wave which represents an irreversible electrode process is due to Zn(II)-tryptophan complex. The rate constant and the product 'an_a' for the electrode reaction have been evaluated.

CHELATES of Pb(II), Cu(II) and Cd(II) with L-tryptophan were first reported by Quintin and Roglizzo¹. Pleticha² has reported polarographic studies of complexes of Co(II), Ni(II), Fe(II) and Mn(II) with several amino acids including L-tryptophan. Chandra and Srivastava³ and Lal and Christian⁴ have also dealt with different aspects of Ni(II)-L-tryptophan system.

The present note deals with polarographic study of Zn(II)-tryptophan system in NaClO₄ as supporting

electrolyte. Sodium perchlorate has been specially used to avoid any possibility of complex formation of Zn(II) with the anion of the supporting electrolyte. The use of buffer has also been avoided for the same reason. Since the kinetic studies were envisaged, use of any surface-active agent has also been avoided.

The d.m.e. (Sargent, USA) had the following characteristics $m^{2/3}t^{1/6} = 2.140 \text{ mg}^{2/3} \text{ sec}^{-1/2}$ in 0.1M NaClO₄ at -0.11 V versus SCE. All the chemicals used were of BDH or E. Merck (AR grade). ZnCl₂ was used as the depolarizer. The experimental set up and the procedure were similar to those reported earlier⁵.

The diffusion coefficients have been experimentally determined using Dawson cell⁶ and 'n' calculated thereafter by Ilkovic equation, corresponding to the first wave has been found to be between 1.7 and 2.2. Such discrepancies in calculated values of 'n' are not unusual⁷.

The potential dependent heterogeneous rate constant $k_{f,h}$ is related to E by the following two relations^{8,9} (1) and (2).

$$k_{f,h} = k_{f,h}^0 \exp[-\alpha n_a F(E + 0.2412)/RT] \quad \dots(1)$$

$$k_{f,h} = KT/h\delta \exp\left[\frac{-\Delta G^\ddagger + \alpha n_a F(E + 0.2412)}{RT}\right] \quad \dots(2)$$

Equating the value of $\log k_{f,h}$ at $E = 0$ from the two relations we get ΔG^\ddagger (kcal) at 25° and is obtained by the relation (3).

$$\Delta G^\ddagger = \frac{-5.706}{4.18} [\log k_{f,h}^0 - 8.16\alpha n_a - 6.79] \quad \dots(3)$$

Zn(II) yields a single well defined wave with $E_{1/2} = -1.0365$ V (versus SCE) and slope 0.040 V in 0.1M NaClO₄. On the addition of tryptophan to the system [1 mM Zn(II), 1 mM tryptophan and 0.1M NaClO₄] the following significant changes are observed in the current-potential curves:

(a) $E_{1/2}$ is shifted to more negative potential and becomes 0.1066 V.

(b) The wave becomes more drawn out with slope = 0.095 V.

(c) The wave is closely followed by a maximum. However, it is not on the rising portion and thus does not interfere with the quantitative study of the wave.

As the tryptophan/Zn(II) ratio is increased keeping Zn(II) constant at 1 mM, the wave records a gradual shift towards more negative potentials till [tryptophan] reaches 5 mM. There is no change at [tryptophan] = 6 mM. This is followed by a positive shift at 7 mM and between [tryptophan] 7 mM to 20 mM, the $E_{1/2}$ remains practically constant.

The height of the maximum gradually decreases with an increase in [tryptophan] till 4 mM and from 4 mM to 6 mM it is reduced to a rounded hump. At 7 mM the rounded hump also disappears and in its place a small second wave appears which changes neither in shape nor in position till 15 mM tryptophan ($i_d = 1.088$ and $-E_{\frac{1}{2}} = 1.225$ V). However, this second wave disappears completely at 20 mM tryptophan.

The fact that on the addition of tryptophan the $E_{\frac{1}{2}}$ is shifted to more negative potentials and

TABLE 1 — IRREVERSIBILITY AND KINETIC PARAMETER DATA

[Tryptophan] (mM)	$E_{3/4}-E_{1/4}$	By Meites and Israel treatment		
		αn_a	ΔG^\ddagger (kcal)	$k_{f/h}^\ddagger$
1	0.130	0.57	28.90	2.3×10^{-11}
2	0.100	0.56	29.49	2.5×10^{-11}
3	0.100	0.57	31.34	2.6×10^{-12}
4	0.120	0.55	27.57	2.0×10^{-10}
5	0.110	0.54	30.45	8.0×10^{-12}
6	0.095	0.53	29.86	1.6×10^{-11}
7	0.090	0.60	31.31	5.6×10^{-12}
8	0.090	0.61	31.63	3.9×10^{-12}
9	0.090	0.58	30.61	1.3×10^{-11}
10	0.090	0.56	31.43	4.2×10^{-11}
15	0.090	0.60	31.46	4.3×10^{-12}
20	0.090	0.53	29.23	4.6×10^{-11}

* α is derived from the relation $E_{3/4}-E_{1/4} = 0.0564/\alpha n$ and $\alpha < 0.5$ at $n=2$ is regarded as a condition for total irreversibility¹¹.

that the slope increased significantly rendering the electrode process from near reversible to totally irreversible (Table 1), indicated a change in basic nature of the reaction and in analogy with Ni(II)-tryptophan system it can be concluded that the first wave corresponds to an irreversible reduction of Zn(II)-tryptophan complex. Similar to Ni(II)-tryptophan system reported by Lal and Christian⁴ there is a second wave also but it is masked by a maximum at lower [tryptophan]. The role of amino acids as maximum suppressors² is already known and as the [tryptophan] is increased in the present study the maximum gradually disappears and the second wave can be observed. However, the concentration of the maximum suppressor (i.e. tryptophan) at this stage is rather high ($7 \times 10^{-3}M$) and possibly because of this the height of the second wave is very much reduced rendering a reliable quantitative study of this second wave at this stage doubtful. At 20 mM tryptophan it is completely eliminated. Studies regarding the origin, nature and kinetics of this wave under alternative experimental conditions are in progress.

The positive shift of the $E_{1/2}$ (first wave) at [tryptophan] > 6 mM may be attributed to the double layer effect¹⁰ due to high [tryptophan]. Tryptophan being charged species in solution (due to zwitterion formation) and also surface-active is quite likely to bring changes in double layer structure which may lead to a positive shift in $E_{1/2}$.

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References

1. QUINTIN, M. & FOGLIZZO, R., *C.r. hebd. Acad. Sci. Ser. C.*, **262** (1966), 1500.
2. PLETICHA, R., *Colln Czech. chem. Commun.*, **15** (1950), 807; *Chem. Listy*, **45** (1951), 185.
3. CHANDRA, S. & SRIVASTAVA, S. N., *Indian J. Chem.*, **7** (1969), 829.
4. LAL, S. & CHRISTIAN, G. D., *J. prakt. Chem.*, **313** (1971), 99.
5. JHA, S. K., JHA, S. & SRIVASTAVA, S. N., *Z. Naturforsch.*, **30b** (1975), 859.
6. ROBINSON, R. A., *Electrolyte solutions* (Butterworths, London), 1955, 33.

7. CHATURVEDI, R. K., *Physico-chemical studies on murexide*, Ph.D. thesis, Agra University, Agra, 1960.
8. MEITES, L., *Polarographic techniques* (Interscience Publishers), 1965, 239.
9. STRASSNER, J. E. & DELAHAY, P., *J. Am. chem. Soc.*, **74** (1952), 6232.
10. MEITES, L., *Polarographic techniques* (Interscience Publishers), 1965, 291.
11. GOTO, R. & TACHI, I., *Proc. Intern. Polarography Congr., Prague*, Vol. 1 (Hrirodovedcke Vydavatelstvi, Prague), 1951, 69.

Thermodynamic Functions & Stability Constants of Some Rare Earths with Phloroglucinol

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Stability constants of the complexes of phloroglucinol with Sc(III), Y(III), La(III), Ce(III), Pr(III) and Nd(III) have been evaluated in aqueous medium at $\mu=0.02M$ ($NaClO_4$), employing Bjerrum-Calvin pH-titration technique, as used by Irving and Rossotti. The values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) accompanying the complex formation have been reported. The order of stability constant is $Sc(III) > Y(III) > La(III)$ and $La(III) < Ce(III) < Pr(III) < Nd(III)$.

IN this note the thermodynamic functions and stability constants of some rare earths with phloroglucinol have been evaluated in aqueous medium.

The methods used were the same as described in previous communications^{1,2}. The practical proton-ligand stability constants and metal-ligand stability constants at various temperatures were obtained employing Bjerrum-Calvin pH-titration technique^{3,4}, as used by Irving and Rossotti⁵.

All the chemicals used were of AR grade. The stock solution (0.01M) of phloroglucinol (E. Merck) was prepared in CO_2 -free doubly distilled water. All other solutions were prepared as described in previous papers^{1,2}. Titrations were carried out under N_2 atmosphere and temperature was maintained with an accuracy of $\pm 0.1^\circ C$.

Titrations were carried out with 0.909M NaOH as in previous papers^{1,2} at $\mu = 0.02M$ ($NaClO_4$); total volume was 100 ml.

The proton-ligand and metal-ligand stability constants were calculated as described in previous papers^{1,2}. The values of stability constants obtained by interpolation at half \bar{n} -values⁵ method are given in Table 1.

The temperature coefficient and Gibbs-Helmholtz equation were used to determine the overall changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS). The total free energy change was obtained from the equation $\Delta G = -RT \ln \beta$, where β is the

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