

Determination of stability constants from diffusion coefficient data

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Abstract. Employing diffusion coefficient data evaluated by improved polarographic techniques, stability constants of Cd^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} with biochemical and chemical ligands using 0.1 M NaClO_4 as supporting electrolyte were determined. The range of β values with biochemical ligands were higher than with chemical ligands. A similar trend of high and low β values was established using the Tanaka plot and Bjerrum's method. Thermodynamic parameters reveal no chelate formation with either biochemical or chemical ligands.

Keywords. Stability constant; diffusion coefficient; formation function; polarography.

1. Introduction

The method of Kacena and Matousek (1953) based on diffusion coefficient data for evaluating stability constants of metal complexes had rarely been applied despite its versatility and its advantages, e.g., (i) it is equally applicable to reversible and irreversible electrode processes with a sound theoretical background, (ii) the calculations are much simpler and involve no term which causes error propagation, (iii) variation in $i_d (= D)$ are more pronounced as compared to changes in $E_{1/2}$; the latter is, in general, difficult to measure with a fair degree of accuracy and is not required in this method. The technique applicable for 1:1 complexation was employed for Cd-protein interaction by the above authors and its validity was confirmed by Zabransky (1959) for Tl-EDTA complexes. The results are comparable with reported data.

The diffusion current was calculated polarographically by simultaneous refinement in $E_{1/2}$ and i_d values evaluated through computerised least-squares method.

The present communication deals with the determination of stability constants of metal ions Zn, Cd, Co and Ni with four ligands—phosphoglyceric acid, phosphoenolpyruvic acid, nitroacetic acid and acetoxyacetic acid. The stability constants were compared with the values obtained separately through the Tanaka plot (Tanaka *et al* 1966) as well as by Bjerrum's method (1941). The thermodynamic parameters (Gupta and Raina 1984), particularly the entropy changes, do not favour chelation.

2. Experimental

2.1 Apparatus

An automatic pen recording polarograph (OH-105 Radelkis, Hungary) with a three-electrode circuitry connected in series with a potentiometer (osaw-India) and a

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conductivity bridge (Philips-India, to serve as indicator for detecting the drawing of heavy current) was employed to record polarograms. The DME had the capillary characteristics $m^{2/3} + t^{1/6} = 2.09 \text{ mg}^{2/3} \text{ S}^{-1/2}$ in 0.1 M NaClO_4 when short circuited. The measurements were made at damping 2, sensitivity $1 \times 10^{-7} \mu\text{A}$ scale division⁻¹, chart speed 2 cm/min, $h = 42$ cm. All the potentials were measured against SCE.

2.2 Chemicals

Phosphoglyceric acid and phosphoenolpyruvic acid (Merck, reagent grade) nitroacetic acid, acetoxyacetic acid and NaClO_4 (SD—AR, purity 99.1–99.5%) were used without further purification. Metal salts were BDH, AnalaR.

2.3 Procedure

A polarographic cell with a three-electrode system was employed for measuring current–voltage curves. 10.0 ml of the solution P_1 (1 mM metal ion + 0.1 M NaClO_4) was measured accurately and placed in the cell and the other solution P_2 (P_1 + ligand) was introduced to P_1 from the microburette. 0.002% Triton X-100 was used as suppressor as and when required.

3. Results and discussion

The diffusion controlled reducing nature of metals was established from (i) i_d vs C (ii) i_d vs $h^{1/2}$ and (iii) low temperature coefficient $1.44\text{--}1.49\%$ deg^{-1} (25 to 40°). The log plots reveal that Zn^{2+} and Cd^{2+} are reduced reversibly while the irreversible nature of the reduction of Co^{2+} and Ni^{2+} was established. The pre-requisites of the present technique are the diffusion controlled reduction and the general applicability of the Ilkovic equation, hence, the reversible or irreversible nature of the electrode process does not affect the calculations. A single complex formation was clearly evident in all cases from the straight line obtained by the $\log C_L$ vs $E_{1/2}$ plots.

A Hi-basic digital computer spectrum (7/DCM, India) with a provision for 36 k byte words of auxillary memory was employed for simultaneous refinement of graphical i_d and $E_{1/2}$ values through the least-squares method (Gupta and Raina 1984). The data on $E_{1/2}$ and i_d resulted in slope values of 29.5 ± 0.4 mV and 29.5 ± 1.0 mV in the case of Cd and Zn respectively, thereby justifying the introduction of the improvements given above.

The modified Ilkovic equation due to Koutecky (1953) was used for calculating diffusion coefficients of metal ions (D_M) and metal complexes (D_{ML}). The following equation has been employed to evaluate β_{ML} ,

$$\bar{D}_{\text{app}} = (D_M + D_{ML}\beta_{ML}(L))/(1 + \beta_{ML}(L)), \quad (1)$$

where (L) is the free ligand concentration, \bar{D}_{app} (the apparent diffusion coefficient corresponding to the total wave height for the simultaneous reduction of M and ML in the mixture), D_M and D_{ML} are the diffusion coefficients of M ions and the ML complex respectively. The limiting value of i_d obtained with the increasing amount of ligand was considered as i_{dML} . By carefully adjusting the ligand concentration, the appropriate condition $i_{dM} = i_{dML}$ (minimum) was set up. The free ligand concentration (L) was

calculated by the straightforward methods reviewed by Leggett (1982). Table 1 reveals the ligand concentrations (L) where i_{dML} was minimum. The value has been reported as i_{dML} from which D_{ML} was calculated. The average of D_M and D_{ML} is \bar{D}_{app} , which subsequently gave β_{ML} . The free and total ligand and metal ion concentrations were used for calculating the Bjerrum function, \bar{n} which in turn provides the stability constant as the intercept on the ordinate from the following equation

$$\bar{n}/(1 - \bar{n})(L) = \beta_1 + \{[(2 - \bar{n})/(1 - \bar{n})](L)\beta_2\}. \quad (2)$$

Table 2 lists the Bjerrum function, \bar{n} , and other parameters for evaluating β_1 for certain representative systems, while β_1 for all the systems studied are shown in table 1.

The stability constants were recalculated by using the total ligand concentration using the equation of Tanaka *et al* (1966). Figure 1 shows the variation of $(C_L/(D_M - \bar{D}_{app}))$ with increasing amounts of C_L (the total ligand concentration), the slope and intercept of which result in β_{ML} .

$$C_L/(D_M - \bar{D}_{app}) = (1 + \beta_{ML}C_L)/\{\beta_{ML} + (D_M - \bar{D}_{ML})\} \quad (3)$$

The β_{ML} values obtained by this method, presented in table 1 fall within 10% of the values resulting from the former two techniques. The contribution of the supporting electrolyte NaClO_4 in promoting or inhibiting complexation is minimum as reported by Beck (1977).

The validity of the set of stability constants calculated by the present method is tested by determining the precision i.e. the average deviation from the mean values (vide table 1). It is evident that the smaller the deviation, the better the corresponding fit. But the inspection of data in this case could not help in deciding which method is better. Preference is given to one developed by Kacena and Matousek (1953) because it describes the process with a lesser number of parameters.

ΔF , ΔH and ΔS have been determined from the following equations

$$\Delta F = -2.303 RT \log \beta_1, \quad (4)$$

$$\Delta H = (-4.576 T_1 T_2 \Delta \log \beta_1)/(T_2 - T_1) \quad (5)$$

and

$$\Delta S = (\Delta H - \Delta F)/T \quad (6)$$

ΔH was also obtained graphically from the slope of the plot $\log \beta_1$ vs $1/T$. The thermodynamic quantities thus calculated on the basis of β values are presented in table 3. As could be seen from the data summarised in the table, the absolute values of ΔF , ΔH and ΔS remain constant for a particular system. The entropy values are lower, in general, for the ligands nitroacetic acid and acetoxyacetic acid, irrespective of the metal ion, as compared with the other two ligands (the highest being in the case of *C*-phosphoenolpyruvic acid); however, the observations of Spike and Parry (1953) indicate that the trend of values do not really favour chelate formation.

In the case of nitroacetic acid and acetoxyacetic acid, the charge neutralization, and consequently, the degree of solvation is comparatively less as compared to phosphoglyceric acid and phosphoenolpyruvic acid. This may induce small changes in solvent orientation and invariably lowers the ΔS , and is thus expected to disfavour the reaction. Low values of β can thus be anticipated.

The ligands, substituted monocarboxylic acid derivatives of acetic acid and propionic acid, used are studied to determine whether the metal linkage is through the

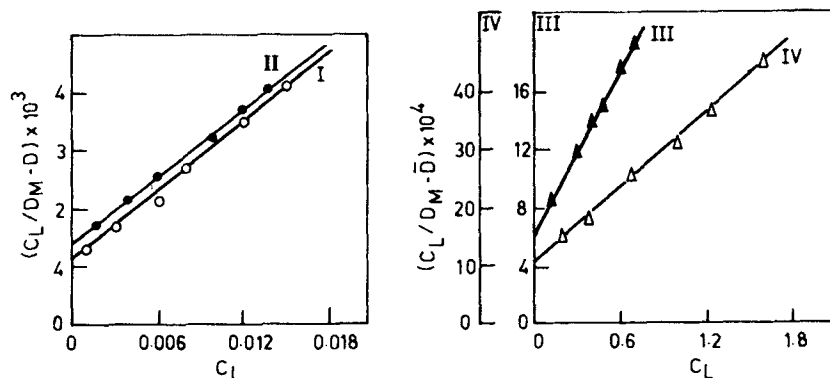
Table 1. Complexes of ligands with metals.

Ligand*	(L)	i_{dML}	$D_{ML} \times 10^{-6}$	$\bar{D}_{app} \times 10^{-6}$	β_{ML}	β (Bjerrum)	β (Tanaka)	β (Mean)	Average deviation from mean	β reported (Martell and Smith 1977)
Zn^{2+} , $i_d = 7.33 \mu A$, $D_M = 8.345 \times 10^{-6} cm^2 s^{-1}$										
PGA	0.0095	1.849	0.531	4.438	105.3	105	111.0	107.1	2.6	2512
PPA	0.0076	1.980	0.608	4.476	131.5	130	133.2	131.5	1.1	912
NAA	0.933	2.565	1.022	4.683	1.07	1.0	1.03	1.03	0.02	1.07
AAA	0.215	2.402	0.896	4.620	4.65	4.5	4.0	4.38	0.26	4.3
Cd^{2+} , $i_d = 7.329 \mu A$, $D_M = 8.345 \times 10^{-6} cm^2 s^{-1}$										
PGA	0.009	4.031	2.524	5.435	118.6	120	120.0	119.5	0.6	2512
PPA	0.012	1.832	0.521	4.433	80.0	80	77.2	79.0	1.3	912
NAA	0.670	2.345	0.854	4.599	1.5	2.0	2.3	1.8	0.3	1.55
AAA	0.080	2.200	0.751	4.548	12.34	12.5	14.3	13.0	0.8	12.6
Co^{2+} , $i_d = 7.153 \mu A$, $D_M = 7.95 \times 10^{-6} cm^2 s^{-1}$										
PGA	0.0075	1.907	0.565	4.257	133.3	135	141.2	136.5	3.46	933
PPA	0.0055	1.920	0.573	4.262	173.1	180	181.8	178.3	3.13	346
NAA	0.891	2.346	0.855	4.403	1.22	1.2	1.93	1.42	0.34	1.0
AAA	0.40	2.20	0.752	4.351	2.43	2.5	3.15	2.36	0.33	2.45
Ni^{2+} , $i_d = 7.176 \mu A$, $D_M = 8.0 \times 10^{-6} cm^2 s^{-1}$										
PGA	0.0083	1.865	0.540	4.270	120.7	120	119.6	120.1	0.40	758
PPA	0.055	2.008	0.626	4.313	178.7	180	20.20	18.7	0.43	219
NAA	0.880	2.510	0.9795	4.489	1.137	1.2	1.57	1.3	0.18	1.15
AAA	0.225	2.534	0.7196	4.35	4.448	4.5	5.93	4.96	0.65	4.26

* PGA = phosphoglyceric acid; PPA = phosphoenolpyruvic acid; NAA = nitroacetic acid; AAA = acetoxyacetic acid.

Table 2. Bjerrum function \bar{n} and data for calculating β_1 .

C_L	(L)	\bar{n}	$[\bar{n}/(1-\bar{n})(L)]$	$[(2-\bar{n})(L)/(1-\bar{n})]$
<i>Zn-phosphoenolpyruvic acid</i>				
0.0052	0.0046	0.60	326	0.016
0.00632	0.0056	0.72	459	0.025
0.00746	0.0066	0.86	930	0.054
0.00852	0.0076	0.92	1513	0.102
<i>Cd-acetoxyacetic acid</i>				
0.0505	0.05	0.52	21.66	0.154
0.0607	0.06	0.68	35.41	0.247
0.0708	0.07	0.85	80	0.536
0.0809	0.08	0.92	144	1.080
<i>Co-phosphoglyceric acid</i>				
0.0051	0.0045	0.60	333	0.016
0.00623	0.0055	0.73	491	0.026
0.00735	0.0065	0.85	871	0.050
0.00845	0.0075	0.95	2533	0.157
<i>Ni-nitroacetic acid</i>				
0.50061	0.50	0.61	3.13	1.78
0.64076	0.64	0.76	4.94	3.30
0.75087	0.75	0.87	8.92	6.51
0.88097	0.88	0.97	36.70	30.21

**Figure 1.** Variation of $[C_L/(D_M - \bar{D}_{app})]$ for Co^{2+} with the total ligand concentration C_L ; I phosphoenolpyruvic acid II phosphoglyceric acid III acetoxyacetic acid IV nitroacetic acid.

oxygen atom of the carboxylate moiety or the oxygen atom of the substituent group(s). It could be inferred from low and high β values that the coordination of the donor atom in case of chemical ligands is different from that of biochemical ligands (in the absence of the chelating effect). In the latter case, the linkage is decidedly through the O atom of a considerably hard base (Ahrland *et al* 1958) of the phosphate group, while the carboxylate moiety is preferentially attached in case of nitroacetic acid and acetoxyacetic acid to give relatively low β values.

Further the low pK values of biochemical ligands as compared to chemical ones

Table 3. Calculated thermodynamic quantities.

T (°C)	β_1	$-\Delta F$ (kcal/mole)	$-\Delta H$ (kcal/mole) calculated	From graph	$-\Delta S$ (cal/deg/mole)
<i>Cd-phosphoglyceric acid</i>					
25	118.6	2.828	—	4.41	5.30
30	106.8	2.812	3.77	4.41	5.27
35	95.0	2.786	4.33	4.41	5.27
<i>Cd-phosphoenolpyruvic acid</i>					
25	80.0	2.595	—	4.46	6.26
30	72.1	2.576	3.73	4.46	6.21
35	63.9	2.544	4.47	4.46	6.22
<i>Cd-nitroacetic acid</i>					
25	1.50	0.240	—	4.43	14.06
30	1.35	0.181	3.78	4.43	14.03
35	1.20	0.111	4.36	4.43	14.02
<i>Cd-acetoxyacetic acid</i>					
25	12.34	1.487	—	4.99	11.76
30	11.04	1.446	3.99	4.99	11.70
35	9.60	1.384	5.18	4.99	11.70
<i>Zn-phosphoglyceric acid</i>					
25	105.30	2.758	—	4.42	5.58
30	94.77	2.740	3.78	4.42	5.54
35	84.30	2.714	4.33	4.42	5.53
<i>Zn-phosphoenolpyruvic acid</i>					
25	131.5	2.889	—	4.44	5.20
30	118.3	2.879	3.80	4.44	5.17
35	105.2	2.849	4.35	4.44	5.16
<i>Zn-nitroacetic acid</i>					
25	1.07	0.040	—	1.15	3.72
30	1.04	0.023	1.02	1.15	3.72
35	1.01	0.006	1.08	1.15	3.71
<i>Zn-acetoxyacetic acid</i>					
25	4.65	0.911	—	4.44	11.84
30	4.19	0.862	3.80	4.44	11.81
35	3.72	0.805	4.36	4.44	11.80
<i>Co-phosphoglyceric acid</i>					
25	133.3	2.897	—	4.18	4.30
30	120.9	2.887	3.51	4.18	4.27
35	108.0	2.866	4.18	4.18	4.26
<i>Co-phosphoenolpyruvic acid</i>					
25	173.1	3.052	—	3.80	2.51
30	156.8	3.039	3.78	3.80	2.51
35	143.0	3.037	3.17	3.80	2.47
<i>Co-nitroacetic acid</i>					
25	1.12	0.067	—	1.66	5.35
30	1.08	0.046	1.31	1.66	5.33
35	1.03	0.018	1.76	1.66	5.33
<i>Co-acetoxyacetic acid</i>					
25	2.43	0.526	—	3.77	10.88
30	2.20	0.475	3.57	3.77	10.87
35	2.01	0.427	3.35	3.77	10.85
<i>Ni-phosphoglyceric acid</i>					
25	120.7	2.839	—	4.39	5.20
30	108.9	2.824	3.72	4.39	5.17
35	96.8	2.799	4.29	4.39	5.16

Table 3. (Continued)

<i>T</i> (°C)	β_1	$-\Delta F$ (kcal/mole)	$-\Delta H$ (kcal/mole) calculated	From graph	$-\Delta S$ (cal/deg/mole)
<i>Ni-phosphoenolpyruvic acid</i>					
25	17.9	1.708	—	4.46	9.23
30	16.1	1.673	3.81	4.46	9.19
35	14.3	1.628	4.40	4.46	9.19
<i>Ni-nitroacetic acid</i>					
25	1.14	0.078	—	1.83	5.88
30	1.09	0.051	1.61	1.83	5.87
35	1.04	0.024	1.74	1.83	5.86
<i>Ni-acetoxyacetic acid</i>					
25	4.45	0.884	—	4.27	11.36
30	4.02	0.837	3.65	4.27	11.33
35	3.59	0.782	4.19	4.27	11.32

depict the major driving force for the charge neutralization process causing the complexation. Jones *et al* (1958) and Clarke *et al* (1963) approved the relationship connected with the basic strength of the ligand and the log of the stability constant by interpreting the π -electron interactions of the metal ligand bond. However, the electron density at the basic centre of the biochemical ligands would almost be the same due to P–O groupings, hence, the stability constants will also be nearly equal. The same would be the case with chemical ligands having C–O bonds. Thus the similarity of β values between the sets of biochemical and chemical ligands is certain and is clearly evident from the observation made herein (vide table 1).

Wold and Ballou (1957) during the interconversion study of 2-glyceric acid 2-phosphate and enolpyruvic acid phosphate attempted to derive an expression containing variations of apparent equilibrium constant with pH and metal concentration. The calculations are deprived of the true equilibrium rigour and hence the validity of data is rather doubtful, subsequently the reported high β values with phosphoglyceric and phosphoenolpyruvic acids (vide the last column of table 1) cannot be considered worth comparing. However, the β values with acetoxyacetic acid and nitroacetic acid are highly comparable e.g., Co-acetoxyacetic acid—reported 2.45, this work 2.43; Cd-nitroacetic acid—reported 1.55; this work 1.5; Zn-nitroacetic acid—reported 1.07, this work 1.07 and so on (table 1).

It can be concluded that the interaction of metal ions with biochemical ligands results in stronger complexes than with chemical ligands.

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