

Complexes by polarography—zinc, copper, lead and indium complexes with mandelic acid

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Abstract. Reduction of the complexes of zinc, copper and lead at the d.m.e. was reversible and the stability constants were determined from the shift in the half-wave potentials in the presence of mandelic acid. Four complexes were identified for zinc and copper with the overall stability constants 25, 125, 490 and 1380 and 100, 3.3×10^3 , 9.6×10^3 and 1.6×10^4 respectively while three complexes were observed for lead with the stability constants 18, 215 and 294. In the case of indium, the reduction of the 'simple' ion is irreversible and that of the complex is reversible and hence the system was studied by the method of Momoki and Ogawa. Four complexes, with the stability constants 8.3×10^2 , 4.0×10^9 were found to exist.

Keywords. Complexes; polarography; zinc; copper; lead; indium; mandelic acid.

1. Introduction

Complexes of metals with acetic acid and its derivatives like glycollic acid (hydroxy acetic acid) glycine (amino acetic acid), etc., have been studied earlier by different methods (Martell and Sillen 1971). Complexes of phenyl substituted acetic acid have, however, not been studied. A polarographic study of the complexes of zinc, copper, lead and indium with mandelic acid, i.e., 2-phenyl 2-hydroxy acetic acid ($C_6H_5-CH(OH)-COOH$)—was, therefore, undertaken.

2. Experimental

The polarograms were obtained with a manual set-up. The capillary had the following characteristics : $m = 1.49 \text{ mg sec}^{-1}$ and $T = 4.30 \text{ sec}$ (in the supporting electrolyte, open circuit). Stock solutions of zinc, copper and lead were prepared from zinc sulphate, copper sulphate and lead nitrate (BDH AnalaR or equivalent) and were estimated by standard methods. A stock solution of indium perchlorate was prepared by dissolving indium metal (BDH, 99.9% pure) in 1 : 1 nitric acid, evaporating to dryness and fuming it repeatedly with perchloric acid. This was estimated by titrating with standard EDTA solution (Welcher 1958). Mandelic acid (Hopkin and Williams) was purified by recrystallisation from hot water.

Reagent grade potassium chloride, potassium nitrate or sodium perchlorate was used as supporting electrolyte. The pH of the solutions was adjusted with potassium hydroxide and was measured with a Beckman Expandomatic SS-2 pH meter. The reported currents have been corrected for the residual current.

3. Results

3.1. Zinc system

Zinc gives a well-defined wave in many supporting electrolytes and the reduction is nearly reversible with the standard rate constant of the order of 10^{-3} cm/sec (Tanaka and Tamamushi 1964). The half-wave potential in 1 M potassium chloride was obtained as -1.0065 V vs SCE and the slope of 32 mV for the log-plot indicated reversible reduction. Polarograms of 4×10^{-4} M zinc were obtained in the presence of different concentrations of mandelic acid, keeping the pH of the solution between 5 and 6. The reduction was reversible as shown by the slope of the log-plots and the decrease in the diffusion current and the shift in the half wave potential to more negative values indicated complexation. Table 1 gives the half-wave potentials as a function of the mandelate ion concentration which was calculated from the pH of the solution and the pK value of 3.00 (Sudersanan 1975) for mandelic acid.

The Fronaeus functions, $F_0(L)$, calculated from the half-wave potentials (DeFord and Hume 1951), were analysed graphically for the stability constants. The values reported here were checked by comparing the F_0 -functions calculated on the basis of these values with the experimental values. Four complexes were identified with the overall stability constants as 25, 125, 490 and 1380.

Table 1. $E_{1/2}$ and F_j functions for zinc-mandelate system.

Zn = 4×10^{-4} M; $\mu = 1.0$ (KCl + ligand)

| (Mandelic acid) <i>M</i> | pH | pL | $E_{1/2}$ - V vs SCE | i_d μA | F_0 | F_1 | F_2 | F_3 | F_4 | F_0 calc |
|-----------------------------|------|------|----------------------------|------------------|-------|-------|-------|-------|-------|---------------|
| 0 | .. | .. | 1.0065 | 2.60 | 1.000 | .. | .. | .. | .. | 1.000 |
| 0.0209 | 4.90 | 1.68 | 1.0115 | 2.36 | 1.615 | 29.45 | .. | .. | .. | 1.584 |
| 0.0443 | 5.15 | 1.35 | 1.0165 | 2.42 | 2.402 | 31.63 | 149.7 | 555.0 | 1467 | 2.417 |
| 0.0886 | 5.80 | 1.05 | 1.0245 | 2.20 | 4.693 | 41.71 | 188.7 | 719.3 | .. | 4.673 |
| 0.1773 | 4.92 | 0.75 | 1.0370 | 2.01 | 13.39 | 69.87 | 253.1 | 722.4 | 1311 | 13.58 |
| 0.2659 | 5.12 | 0.58 | 1.0480 | 1.92 | 32.54 | 118.7 | 352.4 | 855.3 | 1374 | 31.84 |
| 0.3546 | 5.30 | 0.45 | 1.0575 | 1.86 | 69.58 | 193.4 | 475.0 | 987.2 | 1403 | 69.52 |
| 0.3920 | 5.67 | 0.41 | 1.0615 | 1.88 | 93.50 | 235.9 | 537.9 | 1053 | 1436 | 90.28 |
| 0.4900 | 5.82 | 0.31 | 1.0695 | 1.81 | 179.2 | 363.7 | 691.1 | 1155 | 1357 | 180.5 |

$$\beta_1 = 25; \beta_2 = 125; \beta_3 = 490; \beta_4 = 1380.$$

3.2. Copper system

The reduction of copper at the dropping mercury electrode was reversible both in the presence and in the absence of mandelic acid. The half-wave potentials of copper are reported in table 2 as a function of the ligand concentration along with the F_j -functions. Graphical solution of these functions proved the existence of four species with the stability constants 100, 3.3×10^3 , 9.6×10^3 and 1.6×10^4 .

3.3. Lead system

The lead complexes with mandelic acid were reduced reversibly at the d.m.e. The half-wave potentials and the F_j -functions are reported in table 3. Three complexes were observed with the stability constants 18, 215 and 294.

3.4. Indium system

The polarographic reduction of indium is irreversible in non-complexing media but the reduction becomes reversible in the presence of strong complexing agents (Moorhead and MacNevin 1962). As the reversible half-wave potential for uncomplexed indium cannot be measured, the method of DeFord and Hume cannot be applied for the evaluation of the stability constants. A modified approach (Momoki and Ogawa 1971) was, therefore, adopted which is outlined below.

Table 2. $E_{1/2}$ and F_j functions for copper-mandelate system.

| Cu = 4×10^{-4} M; $\mu = 1.0$ (KNO ₃ + ligand) | | | | | | | | | | |
|--|------|-------|-------------------------|---------------|-------|-------|-------|-------|-------|------------|
| (Mandelic acid) M | pH | pL | $E_{1/2}$ - V vs S.C.E. | i_d μ A | F_0 | F_1 | F_2 | F_3 | F_4 | F_0 calc |
| 0 | .. | .. | -0.0210 | 2.70 | .. | .. | .. | .. | .. | .. |
| 0.0101 | 4.30 | 2.024 | -0.0125 | 2.27 | 2.281 | 135.5 | 3756 | .. | .. | 2.248 |
| 0.0202 | 4.65 | 1.708 | -0.0045 | 2.24 | 4.269 | 167.0 | 3424 | .. | .. | 4.293 |
| 0.0401 | 4.50 | 1.415 | 0.0065 | 2.12 | 10.47 | 246.0 | 3794 | .. | .. | 10.32 |
| 0.0600 | 4.82 | 1.230 | 0.0150 | 2.04 | 20.88 | 340.0 | 4080 | .. | .. | 20.45 |
| 0.0833 | 5.15 | 1.084 | 0.0225 | 2.00 | 37.79 | 446.2 | 4199 | 10900 | 15763 | 37.82 |
| 0.1110 | 5.25 | 0.958 | 0.0300 | 1.97 | 68.06 | 608.1 | 4608 | 11860 | 20490 | 67.41 |
| 0.1388 | 5.35 | 0.860 | 0.0360 | 1.96 | 108.6 | 779.8 | 4926 | 11790 | 15870 | 108.7 |
| 0.1704 | 5.28 | 0.772 | 0.0435 | 2.04 | 171.7 | 1009 | 5373 | 12260 | 15721 | 172.0 |
| 0.2016 | 5.30 | 0.698 | 0.0475 | 2.07 | 247.9 | 1232 | 5650 | 11730 | 10629 | 256.4 |
| 0.2520 | 5.35 | 0.601 | 0.0545 | 1.96 | 447.8 | 1783 | 6719 | 13650 | 16168 | 446.9 |
| 0.3000 | 5.50 | 0.525 | 0.0605 | 1.95 | 713.6 | 2385 | 7647 | 14550 | 16566 | 709.3 |
| 0.3331 | 5.35 | 0.480 | 0.0645 | 1.97 | 957.0 | 2888 | 8422 | 15470 | 17729 | 936.2 |
| 0.4008 | 5.15 | 0.401 | 0.0700 | 1.94 | 1485 | 3736 | 9152 | 14730 | 12912 | 1562 |

$$\beta_1 = 100; \beta_2 = 3300; \beta_3 = 9600; \beta_4 = 16000$$

Table 3. $E_{\frac{1}{2}}$ and F_j -functions for lead-mandelate system.

| Pb = 4×10^{-4} M; $\mu = 1.0$ (KNO ₃ + Ligand) | | | | | | | | | |
|--|------|--------|--------------------------------------|------------------|-------|-------|-------|-------|---------------|
| (Mandelic Acid) <i>M</i> | pH | pA | $E_{\frac{1}{2}}$ - V vs SCE | i_d μA | F_0 | F_1 | F_2 | F_3 | F_0 Calc |
| 0 | .. | .. | 0.4030 | 2.71 | .. | .. | .. | .. | .. |
| 0.0400 | 3.28 | 1.6263 | 0.4075 | 2.51 | 1.524 | 22.16 | 197.1 | .. | 1.530 |
| 0.0400 | 5.20 | 1.4013 | 0.4110 | 2.40 | 2.084 | 27.32 | 247.4 | .. | 1.875 |
| 0.0800 | 5.40 | 1.0991 | 0.4190 | 2.40 | 4.154 | 39.63 | .. | .. | 3.887 |
| 0.1600 | 3.30 | 1.0163 | 0.4200 | 1.86 | 4.964 | 41.15 | 245.6 | 317.7 | 4.922 |
| 0.1600 | 5.15 | 0.7996 | 0.4310 | 2.21 | 10.48 | 59.75 | 266.3 | 323.3 | 10.32 |
| 0.2400 | 5.25 | 0.6227 | 0.4400 | 2.14 | 21.56 | 86.26 | 288.5 | 308.3 | 21.29 |
| 0.3200 | 5.40 | 0.4970 | 0.4460 | 1.95 | 37.50 | 114.7 | 305.3 | 283.6 | 37.74 |
| 0.4000 | 5.75 | 0.3988 | 0.4525 | 1.99 | 60.40 | 148.8 | 329.0 | 285.6 | 60.79 |
| 0.5000 | 5.45 | 0.3029 | 0.4590 | 1.90 | 104.0 | 206.8 | 380.3 | 332.1 | 98.06 |
| 0.6000 | 5.40 | 0.2239 | 0.4633 | 1.85 | 151.0 | 251.2 | 391.3 | 295.2 | 150.5 |

$$\beta_1 = 17.5; \beta_2 = 215; \beta_3 = 294.$$

The expression, derived by DeFord and Hume, may be rearranged as

$$\frac{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 + \dots + \beta_N [L]^N}{i_{d(s)} \cdot \exp \left[\frac{nF}{RT} \cdot E_{\frac{1}{2}(s)} \right]} = \frac{1}{i_{d(s)} \cdot \exp \left[\frac{nF}{RT} \cdot E_{\frac{1}{2}(s)} \right]} \quad (1)$$

The denominator of the left hand side includes $E_{\frac{1}{2}(s)}$, which is experimentally inaccessible and hence is written as an unknown as

$$\frac{1}{i_{d(s)} \exp \left[\frac{nF}{RT} \cdot E_{\frac{1}{2}(s)} \right]} = \beta'_0 \quad (2)$$

The right hand side of (1) can be measured experimentally and is denoted by $F'_{0,s}$ so that

$$\frac{1}{i_{d(s),s} \cdot \exp \left[\frac{nF}{RT} \cdot E_{\frac{1}{2}(s),s} \right]} = F'_{0,s} \quad (3)$$

where $i_{d(s),s}$ and $E_{\frac{1}{2}(s),s}$ are the diffusion current and the half-wave potential of the complex ion at the ligand concentration $[L]_s$. It is seen from equations (1), (2) and (3) that

$$\beta'_0 + \beta'_1 [L]_s + \beta'_2 [L]_s^2 + \dots + \beta'_N [L]_s^N = F'_{0,s} \quad (4)$$

$$\text{where } \beta'_j = \beta'_0 \cdot \beta_j = \frac{\beta_j}{i_{d(s)} \cdot \exp \left[\frac{nF}{RT} \cdot E_{\frac{1}{2}(s)} \right]} \quad (5)$$

For convenience, (4) is divided on both sides by $F'_{0,m}$ obtained at the ligand concentration $[L]_m$, so that

$$\frac{\beta'_0}{F'_{0,m}} + \frac{\beta'_1}{F'_{0,m}} [L]_i + \frac{\beta'_2 [L]_i^2}{F'_{0,m}} + \dots + \frac{\beta'_N}{F'_{0,m}} [L]_i^N = \frac{F'_{0,i}}{F'_{0,m}} = F''_{0,i} \quad (6)$$

that is $F''_{0,i} = \frac{i_{d(e),m}}{i_{d(e),i}} \cdot \exp \left[\frac{nF}{RT} \{E_{\frac{1}{2}(e),m} - E_{\frac{1}{2}(e),i}\} \right]$, (7)

where $E_{\frac{1}{2}(e),m}$ and $i_{d(e),m}$ are the reversible half-wave potential and the diffusion current obtained at the ligand concentration, $[L]_m$, which serves as the reference point. Equation (7) may now be solved for $\beta'_0/F'_{0,m}$ and $\beta'_j/F'_{0,m}$ and dividing the latter by the former β_j , is directly obtained by means of equation (5).

Polarograms of 2.08×10^{-4} M indium in 1 M sodium perchlorate were obtained in the presence of different concentrations of mandelic acid, keeping the pH between 2.7 and 4.0. The waves were well defined and were reversible as indicated by the log-plots having a slope of 21 mV. The half-wave potentials shifted to more negative values with increasing ligand concentration indicating complexation. The presence of hydroxy complexes was precluded since the half-wave potential at any ligand concentration was independent of pH in the range of investigation. The $F'_{0,i}$ functions at different ligand concentrations were calculated from equation (7) (table 4) using the half-wave potential at $[L]_m$ equal to 6×10^{-4} M as the reference. These functions were then analysed graphically for the parameters $\beta'_0/F'_{0,m}$ and $\beta'_j/F'_{0,m}$ from which the stability constants were calculated as explained earlier. Four complexes were identified with the stability constants 8.3×10^2 , 4.0×10^5 , 1.0×10^8 and 1.3×10^9 .

Table 4. F_j'' functions—indium system.

| pA | $E_{\frac{1}{2}}$ -V vs SCE | i_d μ A | F''_0 | $F''_1 \times 10^{-3}$ | $F''_2 \times 10^{-5}$ | $F''_3 \times 10^{-7}$ | $F''_4 \times 10^{-8}$ | F''_0 calc |
|------|-----------------------------------|------------------|---------|------------------------|------------------------|------------------------|------------------------|-----------------|
| 3.22 | 0.5150 | 1.62 | 1.000 | 0.667 | 2.783 | .. | .. | 1.000 |
| 3.00 | 0.5180 | 1.61 | 1.420 | 0.820 | 3.200 | 8.00 | .. | 1.400 |
| 2.70 | 0.5245 | 1.60 | 3.016 | 1.208 | 3.540 | 5.70 | .. | 3.053 |
| 2.52 | 0.5300 | 1.59 | 5.710 | 1.703 | 4.010 | .. | .. | 5.945 |
| 2.40 | 0.5350 | 1.58 | 10.21 | 2.403 | 4.758 | 5.90 | .. | 10.48 |
| 2.30 | 0.5390 | 1.56 | 16.39 | 3.158 | 5.316 | 5.84 | .. | 17.10 |
| 2.22 | 0.5430 | 1.54 | 26.24 | 4.273 | 6.288 | 6.48 | 8.0 | 26.24 |
| 2.10 | 0.5490 | 1.52 | 52.93 | 6.541 | 7.551 | 6.44 | 5.5 | 53.95 |
| 2.00 | 0.5545 | 1.50 | 101.0 | 10.04 | 9.540 | 7.14 | 11.4 | 97.58 |
| 1.92 | 0.5585 | 1.48 | 162.0 | 13.48 | 10.82 | 7.02 | 8.5 | 161.4 |
| 1.82 | 0.5640 | 1.47 | 307.0 | 20.43 | 13.29 | 7.26 | 8.4 | 305.0 |
| 1.70 | 0.5710 | 1.46 | 692.0 | 34.57 | 17.04 | 7.32 | 6.6 | 714.3 |
| 1.60 | 0.5770 | 1.44 | 1396 | 55.82 | 22.13 | 7.89 | 7.6 | 1412 |
| 1.52 | 0.5820 | 1.42 | 2519 | 83.95 | 27.82 | 8.47 | 8.2 | 2498 |
| 1.40 | 0.5890 | 1.40 | .. | .. | .. | .. | .. | .. |

$$\beta'_0/F'_0 = 0.60; \beta'_1/F'_0 = 500; \beta'_2/F'_0 = 2.4 \times 10^8; \beta'_3/F'_0 = 6.0 \times 10^7; \beta'_4/F'_0 = 8.0 \times 10^9.$$

$$\beta_1 = 833; \beta_2 = 4.0 \times 10^5; \beta_3 = 1.0 \times 10^8; \beta_4 = 1.33 \times 10^9.$$

Table 5. Stability constants of mandelic acid complexes.

| Metal | Reference | Method | Temp. °C | Medium | β_1 | β_2 | β_3 | β_4 |
|--------|---|--------------------|----------|-----------------------|-----------|-----------------------|-----------------------|------------------------|
| Zinc | Larsson and Folkesson (1965) | Optical rotation | 20 | 2M NaClO ₄ | 30 | 257 | 384 | .. |
| | Bell and Waind (1951) Present study | Kinetic method | 25 | → 0 | 182 | .. | .. | .. |
| | | Polarography | 30 | 1M KCl | 25 | 125 | 490 | 1380 |
| Copper | Present study | Polarography | 30 | 1M KNO ₃ | 100 | 3300 | 9600 | 16000 |
| Lead | Present study | Polarography | 30 | 1M KNO ₃ | 18 | 215 | 294 | .. |
| Indium | Sudersanan and Sundaram (1976) Present study | Solvent extraction | 30 | 1M NaClO ₄ | 760 | 2.6 × 10 ⁵ | .. | .. |
| | | Polarography | 30 | 1M NaClO ₄ | 833 | 4.0 × 10 ⁵ | 1.0 × 10 ⁸ | 1.33 × 10 ⁸ |

It is also possible to calculate the half-wave potential of the 'simple' metal ion by this method. It can be shown from (2) and (3) that

$$\frac{\beta_0^*}{F_{0,2m}^*} = \frac{i_{d(e), m}}{i_{d(s)}} \cdot \exp \left[\frac{nF}{RT} \{E_{\frac{1}{2}(e), m} - E_{\frac{1}{2}(s)}\} \right]. \quad (8)$$

Assuming that $i_{d(s)} \approx i_{d(e), m}$, the half-wave potential of the 'simple' indium ion was calculated as -0.510 V vs. SCE.

4. Discussion

The stability constants of the various mandelate complexes are presented in table 5 along with the reported values. Copper and lead complexes have been studied for the first time. Larsson and Folkeson (1965) have studied the zinc complexes by the optical rotation method, using the *L*-form of mandelic acid. Their values do not agree with those obtained in the present study, probably due to different experimental conditions. Bell and Waind (1951) found that the kinetic approach gave a higher value for the stability constants for this system as well as others and hence there may be a systematic error in this method. For the solvent extraction studies of indium (Sudersanan and Sundaram 1976), only two species were reported probably because of low concentrations of the ligand used, while four complexes were identified in the present investigation. The stability constants for the first two complexes, obtained by the two methods, however, agree well.

It is seen that substitution in the acetic acid molecule affects the stability of the complexes. The presence of hydroxyl group in glycollic acid enhances the stability of its complexes with copper, lead and zinc (Filipovic *et al* 1968) compared to that of the acetate complexes. Further substitution with a methyl group as in the case of lactic acid decreases the stability. The decrease is more marked when the substituent is a phenyl group as in mandelic acid. The variation in the stabilities, viz., mandelate, < lactate, < glycollate is different from that of their dissociation constants and it may, perhaps, be concluded that steric effects are more significant. The overall stability of the mandelate complexes are also not as high as in the case of chelates suggesting a lack of chelating tendency on the part of mandelic acid.

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