

M. DEODATA AZEVEDO*

RUTE GOMES COSTA

M. TERESA VILHENA

Department of Chemistry
Faculty of Sciences
Lisbon
and
Institute Rocha Cabral*
Lisbon



ORD STUDIES ON ORGANIC ACIDS COMPLEXES

I—Complexes formed by malate and aspartate with molybdenum and uranyl ions

The ORD curves of malate and aspartate at two pH values and those of molybdate-malate, molybdate-aspartate, uranyl-malate, uranyl-aspartate were obtained. The identity of ORD curves with different molar ratios metallic ion/aspartate suggests the existence of only one complex molybdate-aspartate and uranyl-aspartate. With malate, the ORD curves suggest the existence of more than one complex molybdate-malate and uranyl-malate. In four cases the complexation increases ϕ of the carboxylic ion.

1 — INTRODUCTION

Complexation of heavy metals by optically active compounds of biological interest has been the concern of several authors (1-5). In this work it is intended to compare the optical activity of malic and aspartic acids in the presence of both molybdate and uranyl ions. The two acids were chosen in view of their similar structures, differing only by the presence of an amino group in aspartic acid instead of the hydroxyl group of malic acid.

2 — MATERIAL AND METHODS

The experimental data of optical rotatory dispersion (ORD) were obtained with a spectropolarimeter Perkin-Elmer 141 M, equipped with sodium and mercury lamps.

L-malic and L-aspartic acids (ANALAR) were reagents obtained from Sigma Chemical Co., and E. Merck E. G. The metallic ions were employed under the forms of sodium molybdate and uranyl nitrate (pro-analysis) from B. D. H.

In all experiments, Job's method was followed, i.e., the sum of the concentrations of both components was kept constant, while the molar ratios metallic ion/carboxylic ion were increased from 1/9 to 9/1. These conditions were used with the intention of finding a wave length at which a Job's plot would show some inflections points, corresponding to the molar fractions concerning the metallic ion present in a complex.

In all experiments the temperature was 26 °C.

3 — RESULTS

In some cases, the strong absorbancy of some solutions did not allow the correct determination of the optical rotation below certain wave lengths. So, the present results will be limited to the range of wave lengths which permitted an accurate result.

The solutions of malate and aspartate were moderately acidic. Acetic acid and sodium hydroxyde were used to adjust the pH to the chosen value.

3.1 — MOLYBDATE

Figs. 1 and 2 show, respectively, the ORD curves of molybdate-malate, at pH = 3.5 and molybdate-aspartate at pH = 4.6, at three different molar ratios molybdate/carboxylic ion and of the carboxylic ion alone. The main difference between the curves corresponding to malate and those relating to aspartate are as follows:

- a) the maximum value of the molar rotation ($\Phi = \frac{[\alpha]}{M} \times 100$) observed for molybdate-aspartate is only $\Phi = +102^\circ$, at $\lambda = 365.0$ nm,

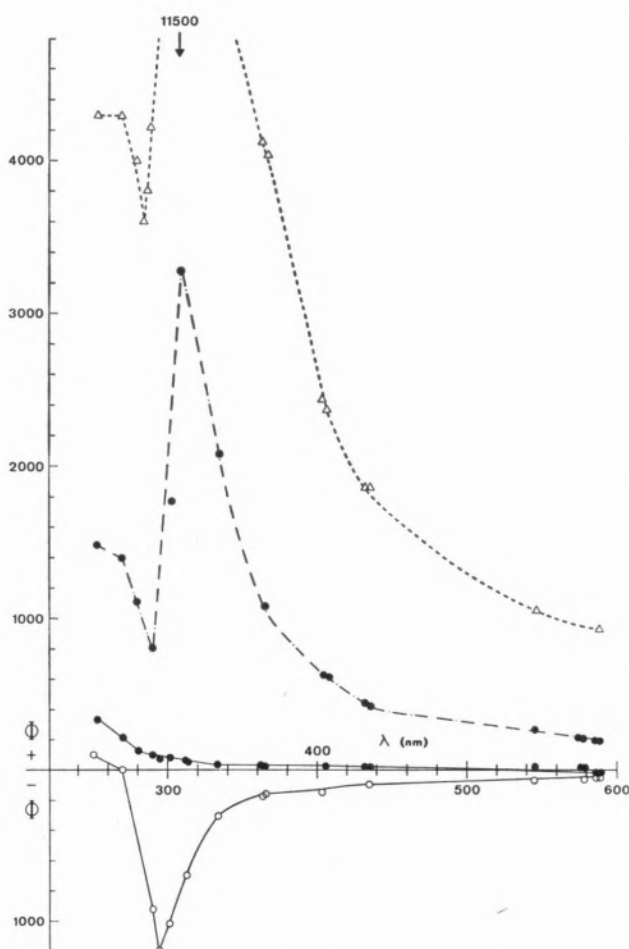


Fig. 1

$[Molybdate] + [Malate] = 0.05M$
pH = 3.5

- Malate 0.05M
- Molar ratio Molybdate/Malate = 3/7
- Molar ratio Molybdate/Malate = 1/1
- △-△- Molar ratio Molybdate/Malate = 7/3

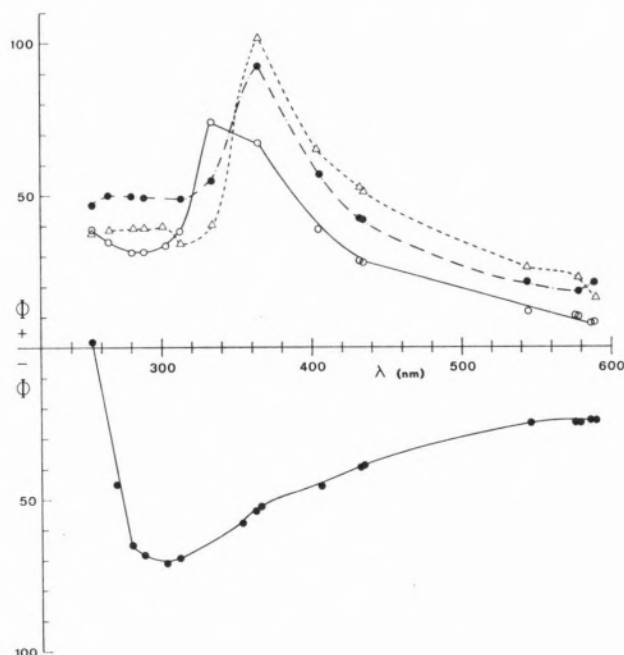


Fig. 2

$[Molybdate] + [Aspartate] = 0.05M$
pH = 4.6

- Aspartate 0.05M
- Molar ratio Molybdate/Aspartate = 1/4
- Molar ratio Molybdate/Aspartate = 1/1
- △-△- Molar ratio Molybdate/Aspartate = 2/1

while for molybdate-malate, at $\lambda = 309$ nm, $\Phi = +11,500^\circ$;

- b) the curves for molar ratios molybdate/aspartate, higher than 1/1 are all identical but with malate the curves present different shapes according to the molar ratios. In any case, a well defined Cotton effect was observed.

3.2 — URANYL

Figs. 3 and 4 present the ORD curves of malate, at pH = 2.7, and aspartate at pH = 3.7, alone and in the presence of three molar fractions of uranyl.

The differences between the ORD curves of malate and aspartate, alone, at two pH values: 2.7 and 3.5 for malate, and 3.7 and 4.6 for aspartate, must be emphasized.

The ORD curves for molar ratios uranyl/aspartate 1/4 and higher values have a peak at the same

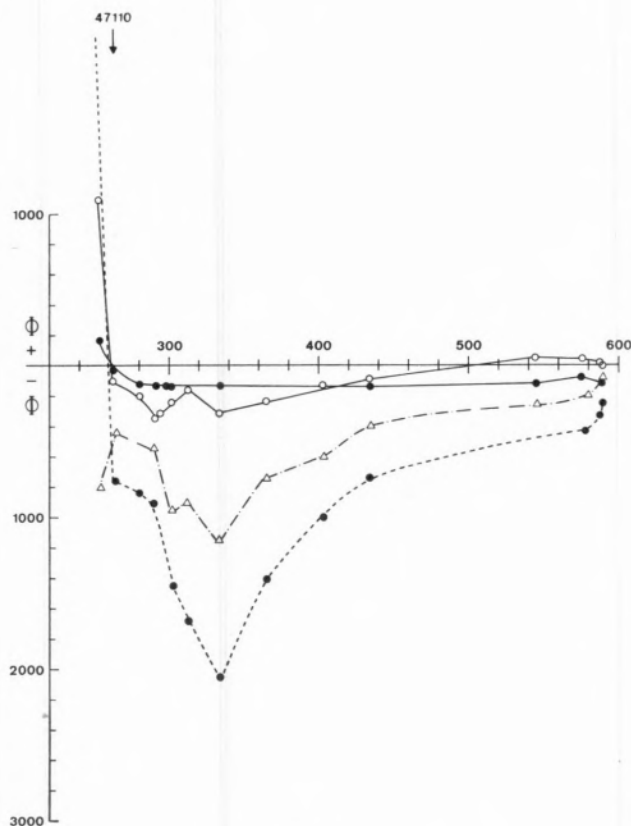


Fig. 3
 $[Uranyl] + [Malate] = 0.01M$
 $pH = 2.7$
 -●-●- Malate 0.01M
 -○-○- Molar ratio Uranyl/Malate = 1/2
 -△-△- Molar ratio Uranyl/Malate = 1/1
 -●-●- Molar ratio Uranyl/Malate = 2/1

wave length ($\lambda = 365$ nm), and Φ increases up to $+282^\circ$ for the ratio 2/1, while for uranyl/malate, between the ratios 1/2 and 2/1, the curves have a through at 335 nm. When the ratio increases, Φ , at this wave length, becomes less negative, but the curves keep almost the same shape. For the carboxylic ions Φ is always smaller, in absolute value, than it is for their complexes (figs. 1-4).

4—CONCLUSIONS

These results show that the substitution of an hydroxyl group by an amino group has a strong influence on the optical activity of the substance. In fact, while the ORD curves of malate, alone,

at $pH = 2.7$, is displaced for negative values of Φ , in relation to the ORD curve of malate at $pH = 3.5$, the opposite effect is observed with aspartate: at the lower pH (3.7) the ORD curve is displaced to less negative values than those of the ORD curve at the higher pH (4.6). In fact, it is known that a solution of an L-amino acid becomes more dextrorotatory (or less levorotatory), as the pH decreases.

The similarity of the ORD curves of molybdate-aspartate for molar ratios higher than 1/1 and of uranyl-aspartate for molar ratios higher than 1/4, can be interpreted as due to the presence on only one complex in each case.

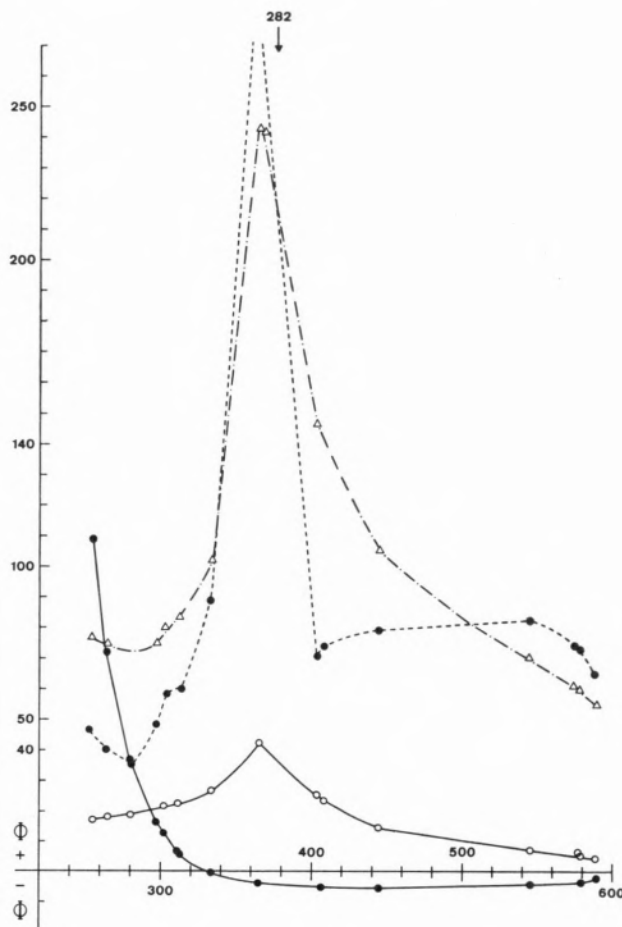


Fig. 4
 $[Uranyl] + [Aspartate] = 0.05M$
 $pH = 3.7$
 -●-●- Aspartate 0.05M
 -○-○- Molar ratio Uranyl/Aspartate = 1/4
 -△-△- Molar ratio Uranyl/Aspartate = 1/1
 -●-●- Molar ratio Uranyl/Aspartate = 2/1

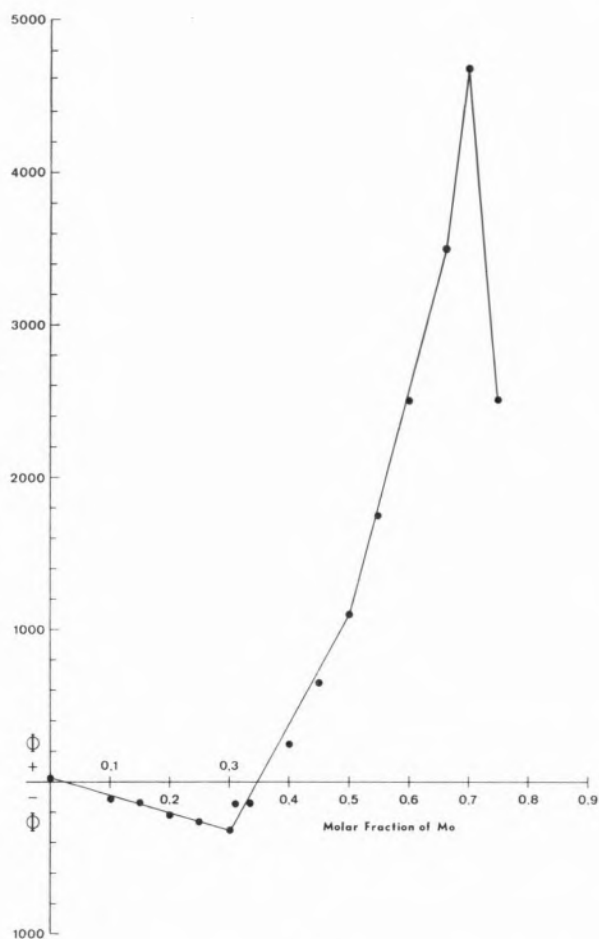


Fig. 5

Job's plot of molybdate-malate at $\lambda = 365 \text{ nm}$; $\text{pH} = 3.5$
 $[\text{Molybdate}] + [\text{Malate}] = 0.05\text{M}$

The large difference between the ORD curves of malate in presence of several molar fractions of either molybdate or uranyl (6) suggest the formation of more than one complex, at least, in molybdate-malate system.

Fig. 5 represents a Job's plot at $\lambda = 365 \text{ nm}$, for several molar fractions of molybdate. The points of maximum and minimum at, respectively, molar fractions 0.3 and 0.7 are in agreement with previous results (4, 5). It suggests the existence of two complexes formed by MoO_4^{2-} and/or by paramolybdate $\text{Mo}_7\text{O}_{24}^{6-}$ ions with malate. The complex behaviour of molybdate ions renders it difficult, at present, to reach any definite conclusion.

Our experimental conditions did not enable us to confirm the existence of molybdate-malate

complexes 1:1 and 1:2 proposed by VOELTER and al. (3), under unknown conditions.

The ORD observed at the wave lengths correspondent to sodium and mercury lamps, in the four cases studied, is not enough to advance hypothesis on probable correlation between the complex conformation and optical activity. However, these are only preliminary results and they will be followed by others obtained at other wavelengths with deuterium and quartz-iodine lamps. We hope, then, to obtain more expanded curves which certainly will allow us to reach further conclusions.

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RESUMO

Obtiveram-se as curvas de dispersão rotatória óptica (ORD) do malato e do aspartato a dois valores de pH e as de molibdato-malato, molibdato-aspartato, uranilo-malato e uranilo-aspartato. A semelhança das curvas com diferentes razões molares ião metálico/aspartato faz admitir a existência de um único complexo molibdato-aspartato e uranilo-aspartato. Pelo contrário, as curvas com malato sugerem a existência de mais do que um complexo molibdato-malato e uranilo-malato. Nos quatro casos estudados a complexação faz aumentar o valor de ϕ do ião carboxílico.