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1:1 Binary Complexes of Citric Acid with Some Metal Ions: Stability and Thermodynamic Parameters

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The stability constants of the 1:1 binary complexes of citric acid with Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Ce^{3+} were determined potentiometrically at 15.0, 25.0 and 35 ºC and at an ionic strength of 0.10 mol L^{-1} ($NaClO_4$). UV-Vis spectroscopic studies were also performed in order to confirm the complex formation and the stability constants of Cu-citric acid system determined potentiometrically. The thermodynamic parameters, ΔG^o, ΔH^o and ΔS^o were reported for the complexes formation reactions. The enthalpy and entropy changes of all binary complexes are positive.

Key Words: Citric acid, Binary complexes, Stability constants, Potentiometric titration.

INTRODUCTION

The studies on complex formation between metal ions and various ligands (especially biologically important ligands), have received considerable attention for a long time. Using such as potentiometric, spectrophotometric, polarographic methods the stabilities of most of these complexes in aqueous solution have been reported. A large number of experimental data have been accumulated in this way. But majority of these data are only at room temperature (*ca.* 20 or 25 ºC). However in order to explain the nature of bonding in the metal complexes, further information may be obtained from the thermodynamics of their formation. For this reason the stability constants should be determined at different temperatures.

Citric acid is chosen as ligand in this work. It is important compound in nature and present in many natural products. It is extensively used in food and pharmaceutical industries. In pharmaceutical industry it is an ingredient for the preparation of a large number of pharmaceutical formulations because of its blood preservative and taste improver properties.

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In the present work, performing potentiometric pH titrations, the formation of 1:1 binary complexes of citric acid with Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} and Ce^{3+} metal ions (hereafter the charge will be omitted to prevent confusion) were studied in aqueous solution at 15, 25 and 35 ºC and constant ionic strength ($I = 0.1$ mol L^{-1} $NaClO_4$) according to Irving-Rossotti's method[1]. The free energy, enthalpy and entropy changes associated with the formation of the metal complexes of cit were calculated. The results were tried to explain according to the HSAB theory. On the other hand, UV-Vis spectroscopic studies were also performed at pH 4 and 25 ºC in order to identify complex species formation. But only the stability constants of the Cu-citrate complexes could be calculated applying to Job's method.

EXPERIMENTAL

Sodium perchlorate, perchloric acid, sodium hydroxide (titrisol), the nitrate salts of maganese(II), cobalt(II), nickel(II), copper(II) and cerium(III), citric acid were of analytical–reagent grade and were provided by Merck AG, Darmstadt, Germany. Bidistilled and CO_2-free water was used throughout. The aqueous stock solutions of corresponding metal salts (0.010 mol L^{-1}) were standardized by titration with EDTA. A standard aqueous stock solution of citric acid (0.010 mol L^{-1}) was prepared daily and stored in the dark.

Potentiometric measurements of the pH were performed on an automatic titrator (Schott Titroline alpha and Radiometer TIM 860 Titration Manager) with a pH combination electrode (Schott BlueLine 11 pH and Red Rod PHC2085). The electrode was also equipped with a temperature probe. Its accuracy was ± 0.1 ºC. The electrode system was calibrated daily with buffer solutions prepared from Merck AG buffer powders at pH 4 and 7 at 25 ºC.

Potentiometric titrations were carried out in a water-jacketed cell of 100 mL fitted with a special cover, through which could be inserted the tip of titrator's dosing unit, the electrode and nitrogen inlet and outlet tubes. Rapid mixing of the solution was achieved by means of a magnetic stirrer. By circulating water from a thermostat (Grant W 14) through the cell's jacket; the temperature of the solution to be titrated was kept constant with an accuracy of ± 0.1 ºC.

The experimental procedure involved the potentiometric titrations of the solutions listed below:

(a) $HClO_4$ (10.0 mmol L^{-1})

(b) $HClO_4$ (10.0 mmol L^{-1}) + citric acid (2.0 mmol L^{-1})

(c) $HClO_4$ (10.0 mmol L^{-1}) + citric acid (2.0 mmol L^{-1}) + M(2.0 mmol L^{-1})

M is any five metal ions used in this work. The total volume of each solution was 50 mL. The ionic strength of solutions was maintained constant at

0.10 mol L^{-1} by the addition of an appropriate amount of 1.0 mol L^{-1} sodium perchlorate stock solution. The titrations were carried out in an inert atmosphere by bubbling purified nitrogen through the solutions. For each solution at least five replicate titrations were made. All the potentiometric titrations were made over the pH range 2-11.

UV-Vis spectroscopic studies were performed on a double-beam UV-Vis spectrophotometer (Shimadzu UV–2100 S) equipped with a water-jacketed cell-holder at 25 ºC (± 0.2 ºC).

Applying Job's method to the suitable M-citric acid systems the stability constant of 1:1 binary complexes may be found spectrophotometrically. For this purpose equimolar solutions (20.0 mmol L^{-1}) of two reactants were made up and mixed in volume ratios 1:5, 2:4, …, 5:1 (total reactant concentration is the same in each case). The maximum absorbance (A) of each solution included complex was measured at pH 4.

Calculations

The protonation constants (pK_as) of the ligand and the stability constants of 1:1 binary M-citric acid complexes were calculated from the potentiometric pH titrations data of the solutions (a)-(c) listed above according to Irving and Rossotti's method[1]. The procedure adopted and the mathematical expressions for the calculations were given below[2,3].

In order to calculate pK_as of the ligand, first the average proton-ligand formation number, n_A, at various pH were determined by following equation:

$$n_A = p - \frac{(\nu_1 - \nu_2)([B] + [A]_o)}{(V_o + \nu_1)[L]_o}$$

where, [B]/mol dm^{-3}: concentration of NaOH titrisol = 1.00×10^{-1}, $[A]_o$/mol dm^{-3}: initial concentration of $HClO_4$ solution = 1.00×10^{-2}, $[L]_o$/mol dm^{-3}: total ligand concentration = 2.00×10^{-3}, V_o/cm^3: volume of solution to be titrated = 50.0, ν_1 and ν_2/cm^3: volumes of NaOH for the solutions (a) and (b) for the same pH value, p: number of dissociated hydrogen of the ligand. The values of pK_as, were calculated with a personal computer *via* a proper software (MS Excel) at n_A = 0.5, 1.5, ...[2,3].

For the calculation of stability constant of the complexes, the average metal-ligand formation number, n_L, at various pH were determined by following equation:

$$n_L = \frac{(\nu_3 - \nu_2)([B] + [A]_o + [L]_o(p - n_A)}{(V_o + \nu_2)n_A[M]_o}$$

where, $[M]_o$/mol dm^{-3}: total metal concentration = 2.00×10^{-3}, ν_3/cm^3: is the volume of NaOH for the solutions (c) for the same pH value as that of ν_1 and ν_2 and the other symbols are the same as above. Then pL (the free ligand exponent) values were calculated using the equation:

$$pL = \log \frac{(1+\beta_1[H^+]+\beta_2[H^+]^2+\beta_3[H^+]^3+...)}{[L]_o - n_L[M]_o}$$

Here, $\beta_1 = K^{H}_{HL}, \beta_2 = K^{H}_{HL}K^{HL}_{H_2L}, \beta_3 = K^{H}_{HL}K^{HL}_{H_2L}K^{H_2L}_{H_3L}, ...$

For the corresponding values of n_L and pL, the formation curve of the metal-ligand system is drawn and the stability constants are calculated with a PC *via* a proper software (MS Excel) at $n_L = 0.5$[2,3].

The values of enthalpy change, ΔH^o, were estimated from the temperature coefficient of the stability constants. Assuming that ΔH^o is constant in the range of temperature studied, the ΔH^o values of the ligand protonation and complex formation reactions were calculated from the relationship:

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^o}{R}$$

The free energy changes, ΔG^o and the entropy changes, ΔS^o, were calculated from the stability constants according to the equations

$$\Delta G^o = -RT \ln K \quad \text{and} \quad \Delta G^o = \Delta H^o - T\Delta S^o$$

where; ln K: stability constant, R: gas constant (8.314 J K^{-1} mol^{-1}), T/K: temperature. As it is well known in Job's method the stability constant of 1:1 binary complexes is

$$K = \frac{A/\varepsilon l}{\{[M]-(A/\varepsilon l)\}\{[L]-(A/\varepsilon l)\}}$$

Here, ε: extinction coefficient, A: absorbance, l: the optical path length in the cell, [M]: metal ion and [L]: ligand concentrations. Rearranging this equation in a linear form, ε and K were calculated easily from the slope and intercept values of the line.

RESULTS AND DISCUSSION

Proton-ligand systems

The protonation constants of citric acid were determined under the condition of the present work. The potentiometric titration curves at 25 ºC are shown in Fig. 1 ('A' and 'A+citric acid' curves). Similar titration curves were obtained at the other temperatures studied. Each curve shows an inflection at a point corresponding to the concentration of protons dissociated as expected (citric acid gives three protons)[4]. The moles of NaOH (m) added before and after neutralization of $HClO_4$ are also indicated in the graphs. The buffer region between m = 0 and 3 indicates that the neutralization of three protons dissociated successively from three –COOH groups of citric acid. Average protonation degree of citric acid *vs.* pH and the mol fractions of the species derived by citric acid *vs.* pH is presented in Fig. 2 and 3, respectively. The values of protonation constants determined at 15, 25 and 35 ºC are listed in Table-1. They are in good agreement with that found previously[5] . The corresponding thermodynamic parameters of protonation processes are presented in Table-2.

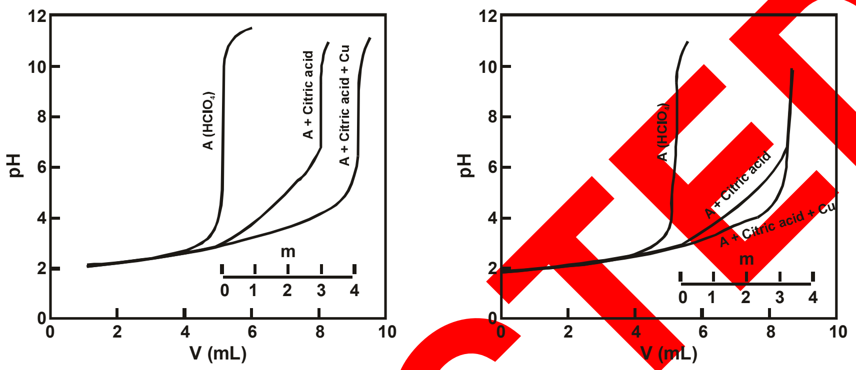

Fig. 1. Potentiometric titration curves of A(HClO$_4$), A + citric acid, A + citric acid + M solutions, upper: for Cu and lower: for Ni (Ce, Co or Mn)

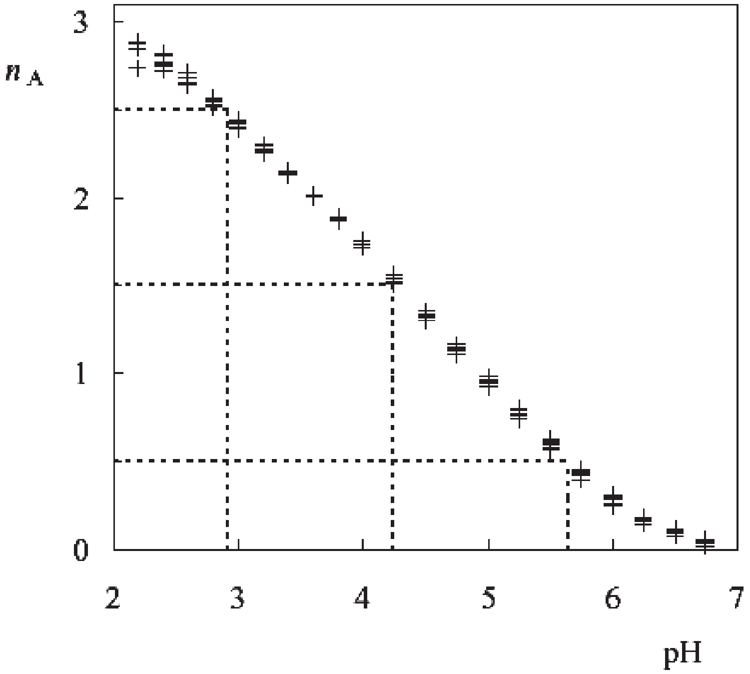

Fig. 2. Average protonation degree of citric acid *vs.* pH (I = 0.10 mol L^{-1} and t = 25 ºC, included the data of four replicate experiments

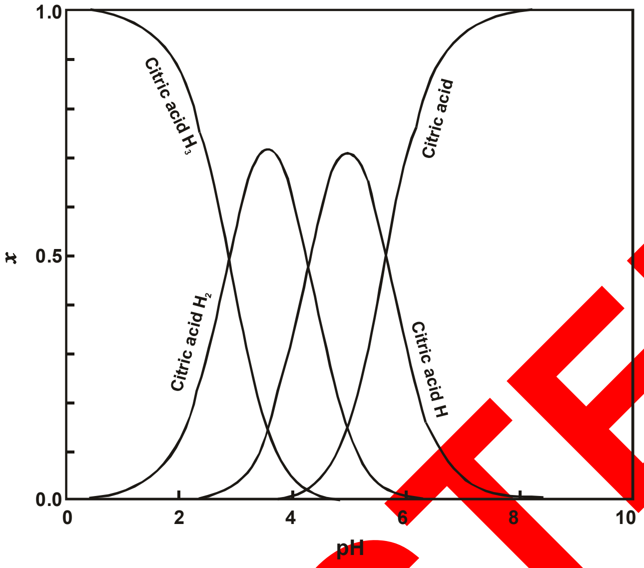

Fig. 3. Mol fractions of the species derived by citric acid *vs.* pH ($I = 0.10$ mol L^{-1} and $t = 25$ ºC)

TABLE-1
PROTONATION CONSTANTS OF CITRIC ACID AT $I = 0.10$ mol L^{-1} ($NaClO_4$)

pK_a	T (ºC)		
	15	25	35
$pK(COOH)_1$	2.81	2.91	2.98
$pK(COOH)_2$	4.14	4.25	4.33
$pK(COOH)_3$	5.52	5.65	5.74

TABLE-2
THERMODYNAMIC PARAMETERS FOR THE PROTON-LIGAND SYSTEMS

pK_a	ΔH^o (J mol^{-1})	ΔG^o (J mol^{-1})	ΔS^o (JK^{-1} mol^{-1})
	(15-35 ºC)	(25 ºC)	(25 ºC)
$pK(COOH)_1$	14	-17	103
$pK(COOH)_2$	16	-24	135
$pK(COOH)_3$	19	-32	171

The ΔH^o value is accurate to ±1 kJ mol^{-1} and ΔS^o value to ±2 JK^{-1} mol^{-1} ($2\alpha = 0.10$).

All the three protonation constants of citric acid increased with increasing temperature as seen in Table-1. Therefore, corresponding enthalpy changes are endothermic (Table-2). Thus, it can be concluded that the higher temperature is favourable for all protonation reactions of the ligand in aqueous solution. As it is well known citric acid is an oxygen donor and its protonation processes are hard-hard interactions according to HSAB theory[6]. As a rule this kind of reaction is entropy-driven. The enthalpy change is positive and counteracts the protonation process as found in this study.

Complex systems

The titration curves of the solution (c) included Cu or Ni at 25 ºC are shown in Fig. 1 (A+citric acid+Cu and A+citric acid+Ni curves). The titration curve of the solution (c) included Co or Mn or Ce was almost the same as that of the solution (c) included Ni. All these titration curves showed enough deviation from those of solution (b) below pH 6 indicating the occurrence of M-citric acid complexes. The color of the solution was light blue for Cu-citric acid, light green for Ni-citric acid, light violet for Co-citric acid, light yellow for Mn-citric acid and colourless for Ce-citric acid systems at pH over 3.5 (up to 6-6.5). The titration curves in Fig. 1 showed that three –COOH groups and –OH (alcoholic) group of citric acid were deprotonated (and neutralized) before and during the Cu-citric acid complexation occurs. But only three hydrogen ions of three –COOH groups were displaced (and neutralized) before and during the Ni-citric acid, Co-citric acid, Mn-citric acid and Ce-citric acid complexation reactions[4]. No precipitation occurred in all of the solutions (c) during the titrations up to pH 6.0-6.5. Average formation degree of M-citric acid complexes in this work *vs.* pH is shown in Fig. 4.

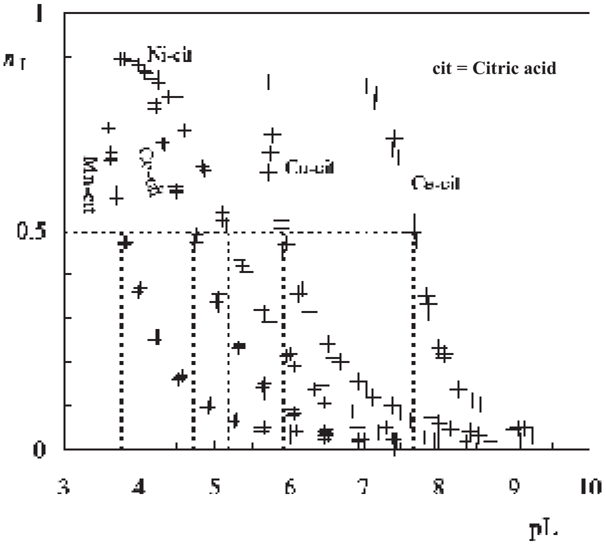

Fig. 4. Average formation degree of M-citric acid complexes *vs.* pH (I = 0.10 mol L^{-1} and t = 25 ºC; included the data of three replicate experiments)

The calculated stability constants of 1:1 binary complexes of citric acid with metal ions employed in this work are presented in Table-3. The corresponding thermodynamic parameters are given in Table-4.

TABLE-3
STABILITY CONSTANTS, log K OF M-CITRIC ACID AT
$[NaClO_4] = 0.10$ mol L^{-1}

System	T (°C)		
	15	25	35
Ce-citric acid	7.52	7.66	7.81
Cu-citric acid	5.81	5.94	6.02
Ni-citric acid	5.09	5.19	5.29
Co-citric acid	4.62	4.74	4.86
Mn-citric acid	3.68	3.77	3.85

log K values are accurate to ± 0.03 log K units ($2\alpha = 0.10$).

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE 1:1
M-CITRIC ACID at $[NaClO_4] = 0.10$ mol L^{-1} AND 25°C

System	ΔH^o (J mol^{-1})	ΔG^o (J mol^{-1})	ΔS^o (JK^{-1} mol^{-1})
	(15-35 °C)	(25 °C)	(25 °C)
Ce-citric acid	25	-44	229
Cu-citric acid	18	-34	174
Ni-citric acid	16	-30	154
Co-citric acid	20	-27	158
Mn-citric acid	14	-22	120

ΔH^o value is accurate to ±1 kJ mol^{-1}, ΔS^o value to ±2 JK^{-1} mol^{-1} ($2\alpha = 0.10$).

The stability constants of the 1:1 M-citric acid complexes in this work are in good agreement with those found previously[5]. They all increase with increasing temperature. The corresponding enthalpy changes are endothermic. The entropy changes are positive in all the cases. These findings may be attributed to the hard acceptor-hard donor interactions in aqueous medium. Thus, citric acid is a hard ligand as mentioned above. In agreement with this the reactions between citric acid and hard acceptors (such as Ce^{3+}) or borderline acceptors (like Cu^{2+}, Ni^{2+} and Co^{2+}) should be characterized by positive entropy and enthalpy changes[6]. It is well known that hard acceptors and hard donors are highly hydrated in aqueous solutions. During complexation, remove of water molecules from hydration layers around acceptor and also donor molecules need a large amount of energy which is not compensated by the energy liberated from new metal-ligand bond formation. Therefore an endothermic reaction occurs. In other words, the complex is entropy stabilized and positive enthalpy change counteracts its formation as found for all M-citric acid complexes in this study.

The order of the stability constants is: Mn < Co < Ni < Cu < Ce. It means that dipositive metal ion complexes follow the Irving-Williams stability series. As it is known the hard acceptors have the higher values of charge/radius ratio[7-9]. The order of charge/radius ratio is almost the same as the order of the stability constants above although the different sources give conflicting values for ionic radii of metal ions in this work.

UV-Vis spectra of Cu-citric acid, Ni-citric acid, Co-citric acid, Mn-citric acidand Ce-citric acid systems and the metal ions at pH 4 in Fig. 5 are verified the complexes formation. Applying Job's method to the Cu-citric acidsystem (suitable data were obtained for this system only) the stability constant of 1:1 Cu-citric acid complex was found as 6.0 (Job plot is in Fig. 6). This is in good agreement with that determined potentiometrically.

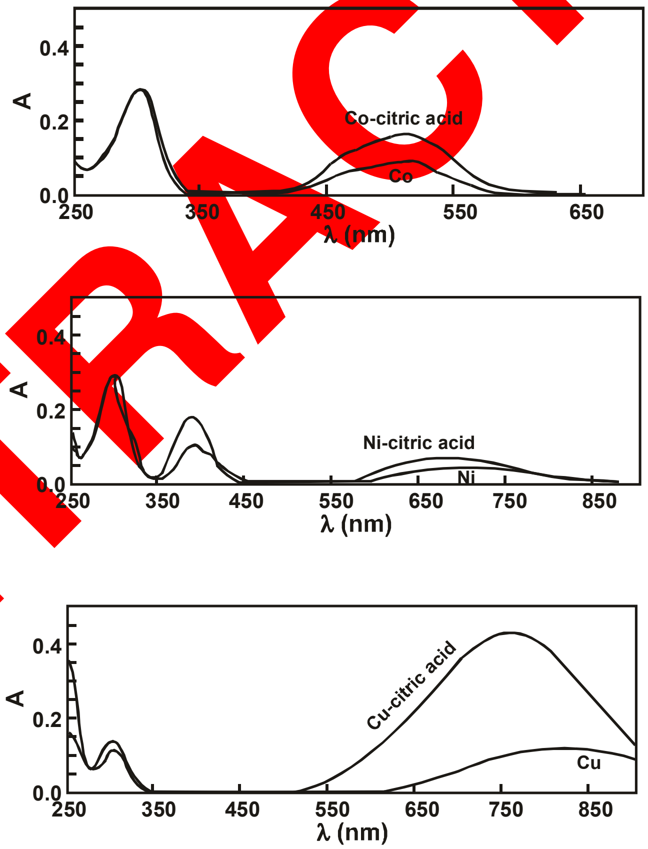

Fig. 5a. UV-Visible spectrum of the aqueous solutions of Co, Ni and Cu metal ions and their cit complexes at pH 4 (c = 2.0×10^{-2} mol L^{-1})

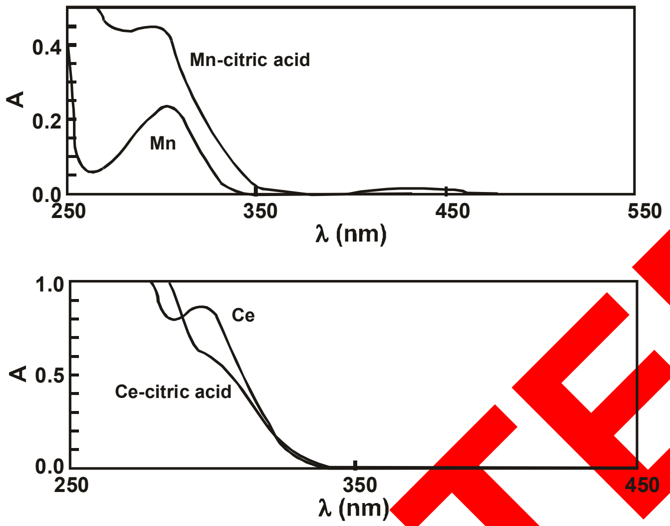

Fig. 5b. UV-Visible spectrum of the aqueous solutions of Mn and Ce metal ions and their citric acid complexes at pH 4 (c = 2.0×10^{-2} mol L^{-1})

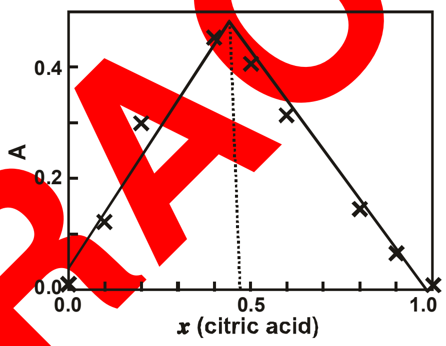

Fig. 6. Job plot for Cu-citric acid complex

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