

Copper, Dioxouranium(VI) & Lanthanide Chelates of Carboxymethylthiosuccinic Acid

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Department of Chemistry, K. K. M. College, Manwath 431 505

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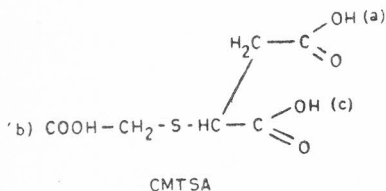
D N SHELKE & D V JAHAGIRDAR*

Department of Chemistry, Marathwada University, Aurangabad 431 004

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Carboxymethylthiosuccinic acid (CMTSA) has three dissociable —COOH groups with pK values 2.91, 3.91, 5.03. Assignment of these values to the different carboxylic groups is given. Cu(II) and UO_2^{2+} chelates with CMTSA have been studied potentiometrically at 30°C and $\mu=0.1M$. The effects of dielectric constant of the solvent medium (dioxane-water) and the ionic strength, on these chelates have been examined. The lanthanides form 1 : 1 and 1 : 2 chelates with CMTSA. The plots of $\log K_1$ and $(\log K_1 + \log K_2)$ versus $e^2/2r$ show a break at gadolinium. The thermodynamic parameters for these chelates have been determined. Smaller values of ΔH show the predominance of the entropy effect in the formation of these chelates.

Metal chelates of a large number of carboxylic, phenolic and naphthoic acids have been investigated in this laboratory in aqueous and mixed solvent media¹⁻³. The ligand acids selected had two closely situated groups and formed chelate rings with a metal ion. It was thought appropriate to extend our studies to a ligand acid molecule having more than two dissociable groups. Carboxymethylthiosuccinic acid (CMTSA, I) fulfils these requirements. This compound appears interesting because the successive pK values of the three dissociable COOH groups, differ by less than one pH unit. The copper, uranyl and lanthanide complexes of CMTSA have been examined pH -metrically in aqueous medium at an ionic strength, $\mu=0.1M$. The nature of the various complexes have been inferred indirectly from the variation of $\log K$ with the square root of the ionic strength.



Materials and Methods

CMTSA (AR, BDH) was purified by repeated recrystallization. The nitrates of Cu (II), rare earths and UO_2 (VI) were all BDH (AR) products. The perchlorates were prepared from the corresponding nitrates⁴. The concentration of metal ions was estimated by the standard procedures⁵⁻⁷. All solutions were prepared in conductivity water ($pH=6.8$; sp.

conductivity= 1.6×10^{-6} mhos). The details regarding other chemicals and measurement of pH were the same as described in earlier papers^{8,9}. Calvin-Bjerrum potentiometric titration technique was adopted to get pK and $\log K$ values.

Results

The acid dissociation constants of CMTSA and stability constants of the metal complexes were calculated by the method of Irving and Rossotti¹⁰. The acid dissociation constants of CMTSA, as obtained from the formation curves were close to each other (2.85, 3.87 and 5.07) and, therefore, the method of pointwise calculation was adopted to get accurate values. The values so obtained (2.86, 3.86, 5.06) do not show any refinement over the earlier ones. pK values obtained by the method of least squares were $pK_1=2.88$; $pK_2=3.89$; and $pK_3=5.02$. The procedure of Block and McIntyre¹¹ was adopted to check these and the calculated pK 's by this procedure were 2.91, 3.91 and 5.03.

The following constants were determined in the present work : (i) $\log K_N$ of Cu (II) and UO_2^{2+} chelates of CMTSA in water and water-dioxane mixtures at 30°C and $\mu=0.1M$ ($NaClO_4$); (ii) $\log K_N$ of Cu (II) and UO_2^{2+} chelates of CMTSA at different ionic strengths (0.049-0.203) in an aqueous medium at 30°C; and (iii) $\log K_N$ of most of the lanthanide chelates of CMTSA at three temperatures (20°, 30° and 40°C) in an aqueous medium at $\mu=0.1M$ ($NaClO_4$).

It was observed that Cu(II) forms 1 : 1 while dioxouranium(VI) forms 1 : 1 and 1 : 2 chelates. The $\log K_1$ and $\log K_2$ values were determined by the method of least squares.

Discussion

Assignment of pK values to various —COOH groups in CMTSA—In an aqueous medium —COOH^(b) will be involved in intermolecular hydrogen bonding with its neighbouring molecule to form a dimer. —COOH^(a) or —COOH^(c) would not possibly be involved in such a type of bonding because these two could form intramolecular hydrogen bond. Because of the electron withdrawing effect of the thio group, —COOH^(c) carbon would be more positive than the carbon atom of —COOH^(a) group. Under these conditions, intramolecular hydrogen bonding would utilize the hydrogen from the —COOH^(c) group. This means the hydrogen of the —COOH^(a) group is unaffected by hydrogen bonding. This suggests that the hydrogen from the —COOH^(a) group would dissociate first and the value of 2.91 should be assigned to it.

The second hydrogen ion might be expected to come from the —COOH^(b) group because intermolecular hydrogen bonding is generally weaker than intramolecular bonding. The —COOH^(c) group would, therefore, be the last one to dissociate.

Effect of dielectric constant on pK and log K values—The pK and log K values of the Cu(II) and UO₂²⁺ chelates of CMTSA, given in Table 1, show that the pK values increase with increase in the dioxane content of the solvent medium. The plots of pK₁, pK₂ and pK₃ against 1/D were nonlinear while those against the mol fraction of dioxane were linear. The slopes of the latter plots were around 10, similar to those obtained earlier for carboxylic acids¹². In the present case the variation in pK values of CMTSA with the dielectric constant of the solvent medium has been compared with that of succinic

acid which is considered as the parent acid. The plot of the first dissociation constant pK₁ was linear with a unit slope with correlation coefficient between 0.96 and 1.0. The plot for pK₂ was also linear but with a slope of 0.6. It can, therefore, be concluded that the effect of the solvent medium is almost identical for all the carboxylic acids in agreement with the observation of Takura *et al.*¹³.

The values of (log K₁—log K₂) have been calculated for UO₂²⁺ chelates of CMTSA in dioxane-water mixtures. It is observed that the difference between log K₁ and log K₂ continuously increases with the increase in dioxane content of the solvent medium. This means that either log K₁ increases or log K₂ decreases as the dielectric constant decreases. A lowering of dielectric constant would increase the electrostatic attraction between the metal ion and the negatively charged or neutral ligand leading to a more stable 1 : 1 complex. The formation of 1 : 2 complex would also be affected.

Effect of ionic strength—It may be inferred from experimental data (Tables 2 and 3) that an increase in the ionic strength of the system causes a decrease in the pK and log K values. The pK₁, pK₂, pK₃, log K₁ and log K₂ values were employed to calculate the thermodynamic constants with the help of the Brönsted equation¹⁴.

$$\log K = \log K^0 - 2AZ_+ Z_- \sqrt{\mu} \quad \dots(1)$$

$$pK = pK^0 - 2AZ_+ Z_- \sqrt{\mu} \quad \dots(2)$$

Since the complexation equilibria involved ions on the reactant and product sides, the Brönsted equation was used in the form

$$\log K = \log K^0 + A\Delta Z^2 \quad \dots(3)$$

Table 1—pK and log K Values of Cu (II) and UO₂²⁺ chelates of CMTSA in Various Dioxane-Water Mixtures [Temp. = 30 ± 0.1°C; μ = 0.1M (NaClO₄)]

System	Constant	Dioxane (% v/v)				
		0	20	40	60	80
CMTSA	pK ₁	2.91	3.49	4.39	5.35	7.65
	pK ₂	3.91	4.56	5.38	6.21	8.38
	pK ₃	5.03	5.55	6.30	7.15	9.08
Cu (II)-CMTSA	log K ₁	4.90	6.04	8.98	11.95	17.95
UO ₂ (II)-CMTSA	log K ₁	4.65	6.20	8.50	11.50	17.97
	log K ₂	3.41	3.57	4.25	5.17	7.60

Standard deviations of pK and log K values = (0.01 to 0.05)

Table 2—pK Values of CMTSA at Various Ionic Strengths in Aqueous Medium at 30°C

Ionic strength (μ)	√μ	pK ₁	pK ₂	pK ₃
0.0000*	0.000	3.38	4.36	5.99
0.0380	0.195	3.08	4.07	5.34
0.0518	0.228	3.01	4.02	5.22
0.0678	0.260	2.98	3.98	5.16
0.0772	0.278	2.94	3.94	5.11
0.0900	0.300	2.91	3.91	5.03
0.1180	0.343	2.80	3.84	4.96
0.1480	0.385	2.72	4.82	4.82

*Theoretical zero ionic strength
Standard deviation of pK values = (0.01 to 0.04)

Table 3—Formation Constants of Cu(II) and UO₂²⁺ Chelates of CMTSA at Various Ionic Strengths (Temp = 30 ± 0.1°C)

Ionic strength (μ)	log K ₁ [Cu(II)]	UO ₂ (II)	
		log K ₁	log K ₂
0.000*	7.10	6.95	4.37
0.049	5.66	5.60	3.78
0.066	5.41	5.25	3.67
0.087	5.25	4.99	3.57
0.099	5.12	4.86	3.48
0.117	4.90	4.65	3.41
0.157	4.60	4.15	3.29
0.203	4.41	3.86	3.15

*pK⁰ and log K⁰ values at theoretical zero ionic strength.
Standard deviation of log K values = (0.01 to 0.03).

Table 4—Dissociation/Association Equilibria and Values of ΔZ²

System	Constant	Reaction equilibria	ΔZ ²	
			Expected	Obs.
CMTSA	pK ₁	H ₃ L ⇌ H ₂ L ⁻ + H ⁺	2	4
	pK ₂	H ₂ L ⁻ ⇌ H ₂ L ²⁻ + H ⁺	4	4
	pK ₃	HL ²⁻ ⇌ L ³⁻ + H ⁺	6	4
	β ₃	H ₃ L ⇌ L ³⁻ + 3H ⁺	12	12
Cu (II)—CMTSA	log K ₁	Cu ²⁺ + H ₂ L ⁻ ⇌ CuLH + H ⁺	-4	-12
		Cu ²⁺ + HL ²⁻ ⇌ CuL ⁻ + H ⁺	-6	-12

Table 5—Formation Constants and Enthalpy and Entropy Changes in Dissociation Equilibria of 1 : 1 and 1 : 2 Rare Earth Complexes of CMTSA
[Temp = 30 ± 0.1°C; μ = 0.1M (NaClO₄)]

Matal ions	log K ₁	log K ₂	−ΔG ₁	−ΔG ₂	−ΔH ₁	−ΔH ₂	+ΔS ₁	+ΔS ₂
La (III)	4.38	3.26	25.42	18.92	4.75	4.37	98.26	76.84
Ce (III)	4.76	3.51	27.62	20.36	4.37	5.16	105.55	84.20
Pr (III)	4.92	3.57	28.55	20.71	4.92	5.27	108.81	85.75
Nd (III)	4.10	3.25	23.79	18.86	4.37	6.13	92.90	82.36
Sm (III)	4.28	3.32	24.83	19.26	5.27	4.41	98.97	78.13
Gd (III)	3.68	3.19	21.35	18.51	6.17	4.41	90.61	75.66
Tb (III)	3.88	3.25	22.51	18.85	4.92	6.28	88.89	83.03
Dy (III)	4.53	3.37	26.28	19.55	4.75	4.41	101.32	79.14
Ho (III)	4.50	3.41	26.11	19.79	4.75	4.41	100.62	79.89
Er (III)	4.71	3.35	27.33	19.44	4.75	4.41	104.58	76.68

ΔH and ΔG : kJ mol⁻¹; ΔS : JK⁻¹ mol⁻¹

$$pK = pK^0 - A \Delta Z^2 \quad \dots(4)$$

where ΔZ^2 is the difference of the square of the charges of product and reactant ions, i. e.

$$\Delta Z^2 = \sum Z^2 \text{ products} - \sum Z^2 \text{ reactants} \quad \dots(5)$$

A literature survey reveals that log K versus $\sqrt{\mu}$ plots are generally linear up to 0.1M ionic strength^{15,16}. The validity of the Brönsted equation was tested for the various systems by plotting pK or log K versus $\sqrt{\mu}$. The mean activity coefficients of sodium perchlorate were taken from Harned and Owen¹² and the ionic strength μ was calculated using the expression :

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad \dots(6)$$

These plots show a very good linear relationship over the entire range of ionic strength except for the last two points corresponding to ionic strengths of 0.157 and 0.203.

Values of ΔZ²—The possible dissociation/association equilibria along with expected/observed ΔZ² values are given in Table 4, the value taken for A being 0.5161 (ref. 17).

It can be seen that the calculated values do not agree with the observed values of ΔZ² except in two cases. The disagreement is much greater in the case of the Cu(II) chelates. The observed ΔZ² was not close to the expected values even using plots of log K versus $\sqrt{\mu}/1 + \sqrt{\mu}$ or $\sqrt{\mu}/1 + \sqrt{\mu} - 0.3\sqrt{\mu}$. The wide discrepancy may be due to an entirely different complexation equilibria being involved.

Rare earth chelates of CMTSA—The rare earths studied formed 1 : 1 and 1 : 2 complexes with CMTSA as is evident from the maximum value of \bar{n} which was around 1.8 for most of the systems. Since the bonding in rare earth complexes is largely electrostatic, stability constants have been estimated using the Born equation. It is expected that log K values should increase linearly with $e^2/2r$. Moeller *et al.*¹⁸ have observed, in general, smooth increase in stabilities with increase in atomic number and decrease in crystal radius, from lanthanum to europium with a discontinuity at gadolinium.

The pK and log K values for the rare earth chelates of CMTSA are set out in Table 5. The plots

of log K₁ versus $e^2/2r$ show a discontinuity at gadolinium. As regards the higher rare earths, occasional minima and maxima have been obtained for the respective chelates. The maxima is more pronounced for 1 : 2 chelates than for 1 : 1 chelates.

The thermodynamic parameters for the lanthanide CMTSA chelates were obtained from the data of pK/log K at three temperatures 20°, 30°, 40°C listed in Table 5. It is seen that the experimental values of ΔH for the —COOH group of CMTSA fall in the range 3.5 to 5.5 kJ mol⁻¹; ΔH for various dicarboxylic acids are of the same order. Our results show that for 1 : 1 chelates the ΔG, owes its value largely to the favourable ΔS, as might be expected from the substantial hydration of the rare earth ions. It can, therefore, be concluded that entropy effect seems to be predominant over the enthalpy effect of the lanthanide chelates of CMTSA. The gadolinium break is seen in ΔH₁ and ΔS₁ values.

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