

DETERMINATION OF MAXIMUM COMPLEXING ABILITY OF WATER-SOLUBLE COMPLEXANTS¹

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INTRODUCTION

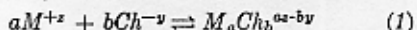
When the maximum complexing ability (MCA) of water-soluble complexants of unknown molecular weight is known, it is possible to calculate the stability constants of metal complexes where these complexants participate (2, 4, 5). Recently (7) MCA has been used to develop new equations which are useful in interpreting stability constants measurements made by the ion-exchange method. These equations define stability constants of anionic or zero-charge metal complexes and could be applied to soil organic matter-metal complexes.

There is no general method for calculating the MCA of a complexant in solution. Several authors (2, 4, 5) have used different procedures, all of which were applicable only to the specific cases being studied. Therefore, the information that could be gained using the equations mentioned above would be only a function of the method used to determine MCA.

MCA represents the potential complexing ability of a solution, that is, its active anionic complexing sites (7). In this paper a general method is proposed to measure MCA of water-soluble complexants that form metallic complexes of anionic or zero charge.

THEORETICAL

The general equation that describes the formation of a complex between a cation M^{+z} and an anionic complexant Ch^{-y} can be stated as follows:



where:

a, b = moles of metal, respectively complexant

y, z = numerical values of their valences

and where: $az-by \leq 0$.

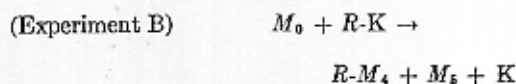
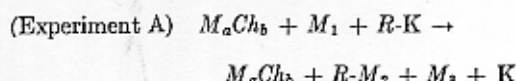
$M_aCh_b^{az-by}$ represents therefore a complex of anionic or zero charge.

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If in equation (1) $M^{+z} \gg Ch^{-y}$, the equilibrium will be shifted to the right and the complexant Ch^{-y} will almost completely form part of the complex M_aCh_b . The proposed method is based on this displacement.

When equilibrium is obtained under conditions described above and a given amount of strong cation exchange resin is added to the system, the resin will bind part of the free M^{+z} cation, thereby decreasing its concentration. This will scarcely affect the dissociation of the M_aCh_b complex, provided the initial M^{+z} concentration is high enough.

If at the same time in a parallel experiment a similar system but without complexant present is used, the following schemes can be derived:



To simplify notation the charges of the ions have been left out.

$R-K$ = strong cation exchange resin saturated in K (similar amounts in Experiments A and B)

M_0 = initial amount of metal added

M_1 = metal in equilibrium with the complex M_aCh_b before adding the resin

$R-M_2$ = metal bound to the resin, after equilibrium, when the complexant is present

M_3 = free metal in solution after equilibrium with resin, when the complexant is present

$R-M_4$ = metal bound to the resin after the equilibrium when the complexant is absent

M_5 = free metal in solution after equilibrium with the resin, when the complexant is absent.

If the initial concentration of metal is much greater than the concentration of the complexant

present in Experiment A, then: $M_1 (=) M_0$, $R-M_2 (=) R-M_4$, and $M_3 (=) M_5$.

Total metal in solution in Experiment B equals M_5 , and total metal in solution in Experiment A equals $(M_3 + \text{complexed metal})$. Since $M_3 (=) M_5$, the complexed metal (M_c) will be very nearly equal to:

$$M_c = (M_3 + M_c) - M_5$$

In this way the moles of metal complexed by the complexant present in Experiment A could be calculated, and therefore MCA of the complexant under study could easily be determined.

All this will be true if the metal concentration is very much higher when compared to the complexant concentration. In this case the decrease in the free metal concentration produced by the resin will affect the dissociation of the complex only in a very slight way. When Experiments A and B are carried out using successively higher concentration of metal ion, a point will be reached where the complexant will be saturated. This saturation will manifest itself when the differences between the total metal in solution of Experiments A and B, after equilibrium with the resin, becomes constant. Starting with this difference, MCA can be calculated.

EXPERIMENTAL

Procedure Adopted to Calculate MCA

An appropriate aliquot of the complexant solution is placed in a 50-ml graduated flask. Ionic strength is then adjusted using a K salt in which the anion does not complex or precipitate the metal under study (we have used 5 ml of 1 N KCl for Zn^{+2} , and 5 ml of 1 N KNO_3 for Cu^{+2} studies). Then an aliquot of a standard metal solution is added. Volume is made up with distilled water and this solution left 16 hr at 25° C with occasional stirring. Twenty-five ml are then taken from this solution and, using a dry flask, put into contact with 1 g of a K-saturated strong cation exchange resin and shaken for 4 hr at 25° C (this time is long enough to attain equilibrium conditions). The supernatant solution is then separated and the total metal not bound by the resin determined. The reference data are obtained in the same manner but without adding complexant solution.

To saturate the complexant, successive experiments were carried out increasing the metal concentration each time until the difference be-

tween the concentration in the problem solution and the reference solution, after equilibrium with the resin, became constant.

The pH of all solutions were adjusted to the required values. In the present work, pH 6.0 was used for Zn^{+2} and pH 4.0 for Cu^{+2} studies.

Using the procedure above, MCA is defined as:

$$MCA = M_c/v \cdot 1000 \quad (2)$$

where

M_c represents the amount of metal complexed by the complexant present (moles) and

v represents the volume of the complexant solution used (ml).

Cu and Zn determinations were performed by atomic absorption spectrophotometry using a Perkin Elmer model 303 spectrophotometer. A procedure of differential spectrophotometry was used (3) to increase the range of useful concentration, maintaining sensitivity and precision. This enhances the accuracy of the measurements of the difference between the metal concentration in the problem solution and the reference solution. In this manner the range for Cu was increased from 20 to 60 ppm and the one for Zn from 3 to 12 ppm.

All experiments were carried out in triplicate and an excellent reproducibility was obtained. The mean values are reported. Reagents used were of analytical grade and all volumetric glassware was of class A.

RESULTS AND DISCUSSION

In order to check this method experimentally, two solutions of known complexants were prepared: (1) $4 \times 10^{-3} M$ tartaric acid and (2) $4 \times 10^{-3} M$ oxalic acid. The complexes of these substances with Cu^{+2} and Zn^{+2} , respectively, were then studied.

As can be seen in Tables 1 and 2, as the initial metal concentration is increased, the complexed metal also increases until a value is reached that is approximately constant when the highest concentrations are used. This results in MCA values that, in the instances of the Cu-tartaric acid complex, correspond to the molar concentration of the active Cu^{+2} complexing sites of the tartaric acid solution employed if a 1:1 molar ratio of Cu:tartaric acid is considered (6). When using oxalic acid the MCA obtained is transformed into molar concentration of active complexing sites by multiplying by 2, since oxalic acid and Zn^{+2} combine in a 2:1 ratio (1).

TABLE 1

Determination of active complexing sites of a 4×10^{-3} M tartaric acid solution with Cu^{+2}

	Initial Cu^{+2} Concentration (Moles/l) $\times 10^3$					
	0.5	1.0	1.5	2.0	2.5	3.0
Cu^{+2} complexed by 1 ml of complexant solution (μg)	63.3	77.6	118.2	244.7	249.8	248.0
Maximum complexing ability (MCA) (moles of Cu^{+2} /l solution) $\times 10^3$	0.98	1.22	1.86	3.85	3.93	3.90
Active complexing sites concentration (moles/l) $\times 10^3$	0.98	1.22	1.86	3.85	3.93	3.90

TABLE 2

Determination of active complexing sites of a 4×10^{-3} M oxalic acid solution with Zn^{+2}

	Initial Zn^{+2} Concentration (moles/l) $\times 10^3$				
	0.8	2.0	4.0	6.0	8.0
Zn^{+2} complexed by 1 ml of complexant solution (μg)	71	125	150	131	137
Maximum complexing ability (MCA) (moles of Zn^{+2} /l solution) $\times 10^3$	1.09	1.91	2.29	2.03	2.10
Active complexing sites concentration (moles/l) $\times 10^3$	2.18	3.82	4.58	4.06	4.20

The molar concentration of active complexing sites obtained with both solutions is very similar to their molar concentration. This means that the MCA values found by this method conform very closely with the real concentration of active sites of the complexing solutions.

The higher the stability of a complex, the lower is the metal concentration that has to be used to attain MCA. The limiting factor in this proposed method is the formation constant of the complex: if this constant is very low, very high concentrations of metal have to be used to reach MCA. This would make analytical determinations of the difference between solutions with and without complexant very difficult.

This method makes possible the determination of MCA of water-soluble complexants whose composition and molecular weight are unknown.

The values obtained will be very close to those corresponding to their complexing sites. Using this method, the equations proposed in a previous paper (7) for the calculation of stability constants would not be affected by arbitrary measurements of MCA. This approach, then, simplifies the use of those equations proposed for the determination of the stability constants of metallic-soil organic matter complexes.

SUMMARY

A general method for calculating the maximum complexing ability of water-soluble complexants forming anionic or zero-charge metal complexes is discussed. The method is based on the saturation of the active anionic complexing sites using successively higher concentrations of metal ion in solution.

Tartaric acid and oxalic acid complexant solutions were used in order to check this method experimentally. Saturating their complexing sites with Cu^{+2} and Zn^{+2} , respectively, it was found that the active complexing sites concentration obtained in both solutions were very similar to their molar concentrations.

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