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Abstract

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ON THE MECHANISM OF INTERACTION OF SPARINGLY SOLUBLE COMPOUNDS WITH COMPLEXONES

At present there are only a few studies of solubility in the presence of the most widespread complexones: ethylenediaminetetraacetic acid (EDTA) and 1,2-diaminocyclohexanetetraacetic acid (^1-4), and in only one case were solubility data used to determine the composition of the complexes formed (^4).

Recently, a large number of works have appeared that consider the theoretical questions of masking by complexones, and various mathematical methods of preliminary calculation have been proposed for a detailed assessment of equilibrium conditions in the system "metal ion–precipitant–complexone." Ringbom introduced the concept of the "conditional solubility product," and conditional constants were used in calculations instead of thermodynamic constants (^5). Cheng proposed the term "selectivity ratio" (S.R.) for assessing the equilibrium state in the system: $S.R. = (pM_p)^2/pM_m$, where pM_p and pM_m are the negative logarithms of the concentrations of the metal ion dissociated from the metal–precipitant and metal–complexing-agent compounds (^6). Hulanicki proposed calculating the "masking coefficient," which is the sum of three factors depending on the properties of the sparingly soluble salt, the efficiency of cation masking, and the efficiency of anion masking, and using it to judge the completeness of the masking reaction (^7). Tanaka introduced the term "ligand buffer" (^8) and considered the course of a precipitation reaction in the presence of this buffer.

Table 1

Solubility of calcium oxalate, magnesium carbonate, and calcium carbonate in the presence of EDTA

Compound	pH	Concentration of all ionic forms of EDTA, mol/L	$[T^{4-}]$, mol/L $\cdot 10^6$	Solubility, a, mol/L $\cdot 10^5$
$CaC_2O_4 \cdot H_2O$	–	–	–	0.24
$CaC_2O_4 \cdot H_2O$	5.10	0.100	0.0541	5.50
$CaC_2O_4 \cdot H_2O$	5.67	0.100	0.504	18.4

Compound	pH	Concentration of all ionic forms of EDTA, mol/L	$[T^{4-}]$, mol/L $\cdot 10^6$	Solubility, a, mol/L $\cdot 10^5$
$CaC_2O_4 \cdot H_2O$	5.70	0.100	0.550	19.9
$CaC_2O_4 \cdot H_2O$	5.88	0.100	0.992	30.1
$CaC_2O_4 \cdot H_2O$	6.25	0.100	1.94	42.4
$CaC_2O_4 \cdot H_2O$	6.28	0.100	2.86	53.4
$CaC_2O_4 \cdot H_2O$	6.54	0.100	4.37	62.2
$MgCO_3$	–	–	–	1.4
$MgCO_3$	5.65	0.030	0.162	4.4
$MgCO_3$	5.65	0.040	0.218	5.5
$MgCO_3$	5.65	0.050	0.271	7.0
$MgCO_3$	5.65	0.060	0.326	8.4
$MgCO_3$	5.65	0.070	0.381	9.6
$MgCO_3$	5.65	0.080	0.435	11.0
$CaCO_3$	–	–	–	0.07
$CaCO_3$	8.29	0.030	27.0	3.0
$CaCO_3$	8.29	0.040	36.1	3.9
$CaCO_3$	8.29	0.050	45.1	4.9
$CaCO_3$	8.29	0.060	54.1	5.9
$CaCO_3$	8.29	0.070	63.2	6.8
$CaCO_3$	8.29	0.080	73.2	7.8

All the proposed computational methods are based on the notion of the independent occurrence of competing precipitation and complex-formation reactions. It is assumed that in all cases the dissolution of a sparingly soluble compound proceeds only through the formation of a simple metal–complexone complex, and in the calculations known values of the instability constants of these complexes are used.

We studied the solubility (at 25±0.1°) of $CaC_2O_4 \cdot H_2O$ and $La_2(C_2O_4)_3 \cdot 9H_2O$ in EDTA and of $La_2(C_2O_4)_3 \cdot 9H_2O$ in 1,2-diaminocyclohexanetetraacetic acid (complexone IV), and also recalculated the literature data on the solubility of $MgCO_3$ and $CaCO_3$ in a solution of the disodium salt of EDTA (^4).

Table 1 gives the dependence of the solubility of $MgCO_3$, $CaCO_3$, and $CaC_2O_4 \cdot H_2O$ (mol/l) on the concentration of the EDTA anion ($C_{10}H_{12}O_8N_2^{-4}$, hereafter denoted T^{-4}). If it is assumed that dissolution of compounds of composition AX may proceed with the formation of simple or mixed complexes, then, in the case of formation of the simple complex $[AT]^{-2}$, its instability constant is given by the expression:

$$K_1 = \frac{[A^{+2}][T^{-4}]}{[AT]^{-2}} = \frac{[A^{+2}][X^{-2}][T^{-4}]}{[AT]^{-2} \cdot [X^{-2}]} = \frac{Pr \cdot [T^{-4}]}{a^2};$$

$$a = \sqrt{\frac{\mathrm{Pr}}{K_1}} \cdot \sqrt{[\mathrm{T}^{-4}]},$$

where a is the solubility of compound AX in the complexone solution (in mol/l).

It is easy to show that, in the case of formation of the mixed complexes $[\mathrm{ATX}]^{-4}$ or $[\mathrm{A(HT)X}]^{-3}$, the solubility depends on the concentration $[\mathrm{T}^{-4}]$ as follows:

$$a = \frac{\mathrm{Pr}}{K_2}[\mathrm{T}^{-4}] \qquad \text{(formation of } [\mathrm{ATX}]^{-4}\text{)};$$

$$a = \frac{\mathrm{Pr}\,[\mathrm{H}^+]}{K_3}[\mathrm{T}^{-4}] \qquad \text{(formation of } [\mathrm{A(HT)X}]^{-3}\text{)}.$$

When a mixed complex is formed, a linear dependence of the solubility a on $[\mathrm{T}^{-4}]$ should be observed (in the case of formation of a protonated complex this is valid at constant pH); when a simple complex is formed, the square of the solubility, a^2, depends linearly on $[\mathrm{T}^{-4}]$.

Analysis of the above solubility data (Table 1) gives grounds to believe that dissolution of $\mathrm{CaC_2O_4 \cdot H_2O}$ proceeds through formation of the complex $[\mathrm{CaT}]^{-2}$; the instability constant calculated by the least-squares method proved to be $10^{-10.7}$ ($\mu = 0.1;\ 25^\circ$), which agrees well with the known value $10^{-10.6}$ (for 20°) ([9]).

In the cited work ([4]), $\mathrm{MgCO_3}$ and $\mathrm{CaCO_3}$ dissolved at a constant pH value (5.65 and 8.29, respectively); therefore the linear dependence indicates formation of mixed complexes, whereas the authors of that work consider the formation of the ions $[\mathrm{MgT}]^{-2}$ and $[\mathrm{CaT}]^{-2}$ to have been proven.

We obtained the following dependence of the solubility of $\mathrm{CaCO_3}$ on the concentration $[\mathrm{T}^{-4}]$ (at pH 8.29):

$$a = 1.1 \cdot 10^2[\mathrm{T}^{-4}] + 8.7 \cdot 10^{-5}\ \text{mol/l}.$$

Our additional investigations showed that, in the disodium salt of EDTA, carbonates dissolve forming the complex ions $[\mathrm{Ca(HT)CO_3}]^{-3}$ and, evidently, $[\mathrm{Mg(TH_2)CO_3}]^{-2}$ or $[\mathrm{Mg(HT)HCO_3}]^{-2}$.

We calculated the overall instability constant for the Ca complex, using the least-squares method (the data were reduced to ionic strength $\mu = 0.1$, and activity coefficients were determined by the Davies equation ([10])):

$$K = \frac{[\mathrm{Ca}^{+2}][\mathrm{H}^+][\mathrm{T}^{-4}][\mathrm{CO_3}^{-2}]}{[\mathrm{Ca(HT)CO_3}]^{-3}} = 2 \cdot 10^{-18}.$$

Figure 1. Thermograms of the compounds $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1) and $Na_4[CaT(CO_3)] \cdot nH_2O$ (2)

Figure 1: Figure 1. Thermograms of the compounds $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1) and $Na_4[CaT(CO_3)] \cdot nH_2O$ (2)

An analogous consideration (because of its complexity, the calculations themselves will be given in a separate communication) showed that dissolution of lanthanum oxalate proceeds with formation of the complexes $[LaT(C_2O_4)]^{-3}$ and $[LaR(C_2O_4)]^{-3}$ (where R is the anion of Complexon IV).

We determined the concentration instability constant of the ion $[LaT(C_2O_4)]^{-3}$ ($\mu = 0.6$-0.73) and recalculated it for zero ionic strength:

$$K_T = \frac{[La^{+3}][T^{-4}][C_2O_4^{-2}]}{[LaT(C_2O_4)]^{-3}} = 8.7 \cdot 10^{-21}.$$

Solid mixed complexes, not previously described by anyone, were also synthesized: $Na_4[MgT(CO_3)] \cdot 4H_2O$, $Na_4[CaT(CO_3)] \cdot nH_2O$, $Na_3[LaT(C_2O_4)] \cdot 5H_2O$, and $Na_3[LaR(C_2O_4)] \cdot 7H_2O$.

Fig. 1. Thermograms of the compounds $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1) and $Na_4[CaT(CO_3)] \cdot nH_2O$ (2)

In the present communication, as an example, we shall consider the properties only of carbonate mixed complexes. Their synthesis was carried out by crystallizing the compounds from solutions of calcium and magnesium carbonates in the presence of the tetrasodium salt of EDTA.

For comparison, by a known procedure ([11]), $Na_2[MgT] \cdot 4H_2O$ and $Na_2[CaT] \cdot 3.5H_2O$ were synthesized. The crystals of $Na_4[MgT(CO_3)] \cdot 4H_2O$ are idiomorphic, with straight extinction, $N_g' = 1.527 \pm 0.003$, $N_p' = 1.515 \pm 0.003$. Perfect cleavage, parallel to the elongation, is sometimes visible.

The crystals of $Na_4[CaT(CO_3)] \cdot nH_2O$ are radial-fibrous or fine-fibrous aggregates; birefringence ~ 0.040, $N_g > 1.515$; $N_p < 1.500$. The crystals of the compound $Na_2[MgT] \cdot 4H_2O$ are ideal rectangular plates, $C = N_g$; $N_g' = 1.545 \pm 0.003$; $N_p' = 1.520 \pm 0.003$.

The compound $Na_2[CaT] \cdot 3.5H_2O$ consists of sheaflike crystals, $N_g = 1.520 \pm 0.003$; $N_p' = 1.510 \pm 0.003$ (all refractive indices were determined by the immersion method)*.

Since the thermal properties of EDTA complexes have been studied very little, and only for three or four simple complexes (see, for example, ([12])), we recorded thermograms of the new compounds (Fig. 1).

Endothermic peaks in the range 100-245° correspond to dehydration. At 380-400° decomposition begins; the difference in the decomposition of the mixed

Figure 2. IR spectra of simple and mixed complexes: $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1), $Na_2[CaT] \cdot 3.5H_2O$ (2), and $Na_4[CaT(CO_3)] \cdot nH_2O$ (3)

Figure 2: Figure 2. IR spectra of simple and mixed complexes: $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1), $Na_2[CaT] \cdot 3.5H_2O$ (2), and $Na_4[CaT(CO_3)] \cdot nH_2O$ (3)

complexes is interesting: in the Mg complex a large exothermic peak is observed at 380–420° (combustion), whereas in the Ca complex the exothermic peak (400°) is barely noticeable against the background of the endothermic peak (390°), apparently associated with the elimination of CO_2. This difference in the course of decomposition evidently indicates a difference in the bonding of the CO_3^{2-} ion in the two complexes.

Fig. 2. IR spectra of simple and mixed complexes: $Na_4[MgT(CO_3)] \cdot 4H_2O$ (1), $Na_2[CaT] \cdot 3.5\ H_2O$ (2), and $Na_4[CaT(CO_3)] \cdot nH_2O$ (3)

To elucidate the character of the bonding of the CO_3^{2-} ion, we recorded the IR spectra of the complexes (Fig. 2). In comparison with the simple complex, in the mixed Mg complex the intensity of the 1450 cm^{-1} peak increases considerably in the re–

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* The refractive indices were determined by A. A. Golovin.

absorption regions of the groups $-COO^-$ and CO_3^{2-}, which may be associated with the inequivalence of the carboxyl groups (upon coordination of the carbonate ion, EDTA may become a penta- or tetradentate ligand and some of the COO^- groups will not be coordinated). In the mixed Ca complex a peak appears at 1510 cm^{-1}, absent in all the other complexes.

Since neither Na_2CO_3 nor $CaCO_3$ absorbs in this region ([13], [14]), this absorption band is not associated with possible impurities.

Analysis of the IR spectra of carbonates and carbonate complexes in which the CO_3^{2-} ion is a mono- or bidentate ligand showed that complexes with monodentate CO_3^{2-} are characterized by absorption bands in the regions 850–870 cm^{-1}, 1025–1070 cm^{-1}, 1460–1500 cm^{-1}, whereas bidentate complexes are characterized by 821–839 cm^{-1}, 1260–1292 cm^{-1}, 1590–1643 cm^{-1} ([15-17]).

The presence of the 1510 cm^{-1} absorption band in the Ca complex indicates that the CO_3^{2-} ion enters the inner sphere of the complex and is coordinated as a monodentate ligand. All the other characteristic absorption bands coincide with the absorption bands of the –COO groups, as well as of C–N and C–H vibrations.

In the complexonate $Na_4[MgT(CO_3)] \cdot 4H_2O$ the CO_3^{2-} ion is probably a bidentate ligand; in the complexonate $Na_4[CaT(CO_3)] \cdot nH_2O$ it is monodentate.

Our solubility studies show that the interaction of sparingly soluble compounds

with solutions of complexones in many cases proceeds with the formation of mixed complexes (entry of the anion of the sparingly soluble compound into the inner sphere of the complex increases its stability). This must be taken into account in complexone masking, and calculation of equilibria in masking can be carried out only if the composition of the complex formed is known in advance. We believe that the proposed methods for calculating masking ([5]-[8]) cannot be used for complexones, since they do not take this into account.

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Note: Figure translations are in progress. See original paper for figures.