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Abstract

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GLASS FORMATION IN SYSTEMS CONTAINING COMPLEXONES

The ease with which supersaturated solutions are formed and the difficulty of crystallizing EDTA complexonates make it necessary, in the synthesis of these compounds, to isolate them from solutions by adding organic solvents (ethyl alcohol, acetone) ([1], [2]). This method is very widespread, and sometimes the only one used in obtaining complexonate crystals; complexonates of alkaline-earth metals are still synthesized only in this way ([2], [3]).

There are data in the literature on the vitrification of concentrated solutions of complexonates. These data are few and concern only compounds of the composition $Ln[LnT]_3$ (where Ln^{3+} is a lanthanide cation, T^{4-} is the EDTA anion) ([4]), as well as certain compounds of other aminopolycarboxylic acids ([5]). The glasses formed have not been studied, nor have the causes of glass formation been investigated.

We followed the crystallization of EDTA complexonates from aqueous solutions: $Na_2[MgT]$, $Na_2[CaT]$, $Na_2[BaT]$, $Na_3H[MgT(CO_3)]$ at 20-25°. In all cases the formation of supersaturated solutions was observed, which then either entirely turned into glass or crystallization proceeded in characteristic rings with an increase in volume. Around these same rings the solution turned into glass. Crystals of the Ca complexonate are the previously undescribed heptahydrate $Na_2[CaT] \cdot 7H_2O$ (H_2O calculated 25.7%; found 25.6%), possessing a fine-fibrous structure; $N_g = 1.594 \pm 0.003$; $N_p = 1.587 \pm 0.003$. Density $d = 1.564$ g/cm^3 (determined in toluene). The glass has the composition $Na_2[CaT] \cdot 5H_2O$ (H_2O calculated 19.8%; found 19.5%), is X-ray amorphous; $N = 1.503 \pm 0.003$; $d = 1.666$ g/cm^3.

For comparison, we synthesized, by the method mentioned above ([2], [3]), the crystalline hydrate $Na_2[CaT] \cdot 3.5H_2O$—bundle-like crystals, $N_g = 1.520 \pm 0.003$; $N_p = 1.510 \pm 0.003$.

Fig. 1. Region of glass formation in the system Na[LaT]—H_4T—NaOH—H_2O. a —crystalline phases, b —glass.

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The IR spectra of the crystals and the glass differ in the region 1330-1360 cm^{-1} (—CH_2—vibrations) and 1250-1290 cm^{-1} (—C—N—and —COO^- vibrations (^{6})). Thermographic study of the crystalline hydrates and glass showed that after dehydration (~160°) all three substances are X-ray-amorphous glass (with refractive index $N = 1.525 \pm 0.003$, sometimes with weak anisotropy), which indicates destruction of the crystal structure upon dehydration. This question will be considered in more detail in a separate communication.

There is a point of view (previously proposed by Schwarzenbach) according to which, in complexes with divalent cations, EDTA is pentadentate, and in aqueous solution the structure of the complex is as follows: $[MeT(H_2O)]^{2-}$ (^{7}). Concentration of the solution may lead to polymerization of the complex through replacement, by an uncoordinated —COO^- group, of the position of coordinated water in another complex ion, with formation of stable chains. The possibility of such chains in a solution of the copper complexonate Na_2[CuT] was discussed in the literature (^{8}), but not

attempt was made to obtain some complexonate in polymerized form. We believe that the supersaturation of the solution and glass formation observed by us are associated with the appearance, in concentrated solutions, of stable chains or a network of complex ions.

The formation of rings and chains cannot but affect the vibration frequencies of the —CH_2—and —C—N—bonds, which apparently accounts for the difference noted above in the spectra of $Na_2[CaT] \cdot 5H_2O$ glass and crystalline hydrates in the region 1250-1360 cm^{-1}.

We found previously unknown regions of stable glass formation in systems of the type complexonate—complexone (acid)—NaOH—H_2O, and examined in detail glass formation in the system Na[LaT]—H_4T—NaOH—H_2O. To construct the physicochemical diagram of the system, the Jänecke-Büke method (^{9}) was used, in which the sum of the amounts of three components (in our case Na[LaT], H_4T, NaOH) is taken to be a constant quantity, while the amount of the fourth component (the solvent) is expressed relative to this sum. The water content in the synthesized glasses and crystalline phases was determined by us only in some cases.

Fig. 1. Region of glass formation in the system Na[LaT]—H_4T—NaOH—H_2O. *a* —crystalline phases, *b* —glass.

In the system considered there is a comparatively narrow region of glass formation, bounded by the limiting compositions of glasses:

Fig. 2. Change in the refractive index of glasses and crystals along the line AB as a function of the NaOH/H_4T ratio

Figure 2: Fig. 2. Change in the refractive index of glasses and crystals along the line AB as a function of the NaOH/H_4T ratio

$$1.7\mathrm{Na[LaT]}\cdot\mathrm{Na_4T}\cdot\mathrm{NaOH}\cdot n\mathrm{H_2O} \rightarrow \mathrm{Na[LaT]}\cdot 3\mathrm{Na_4T}\cdot n\mathrm{H_2O} \rightarrow \mathrm{Na[LaT]}\cdot 1.2\mathrm{Na_2H_2T}\cdot n\mathrm{H_2O}$$

(see Fig. 1). Within the limits of the region we obtained only glasses and were unable to crystallize them; beyond its limits crystallization from saturated solutions occurred, and along the lines *AB* and *CD* the composition of the crystalline phases always corresponded to the composition of the solution, i.e. this part of the system is a region of solid solutions (which is also confirmed by the IR spectra of the crystalline phases).

It was of interest to investigate the glass-crystal transition at the boundary points found. We followed the change in the refractive index of the glass along the line *AB* (Fig. 2), recorded the IR spectra of some glasses and crystals (Fig. 3), and studied them thermographically. The sharp change in the refractive index of the glass on passing from the composition

$$\mathrm{Na[LaT]} \cdot 1.2\mathrm{Na_4T} \cdot 10\mathrm{H_2O}$$

to

$$\mathrm{Na[LaT]} \cdot 1.2\mathrm{Na_3HT} \cdot n\mathrm{H_2O}$$

and

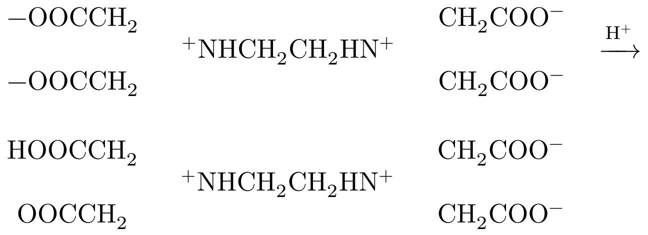
$$\mathrm{Na[LaT]} \cdot 1.2\mathrm{Na_2H_2T} \cdot n\mathrm{H_2O}$$

(Fig. 2) we associate with a change in the internal structure of the glass upon protonation of the anions (here and below we give the gross composition of glasses and crystals, without regard to possible chemical interaction between the components).

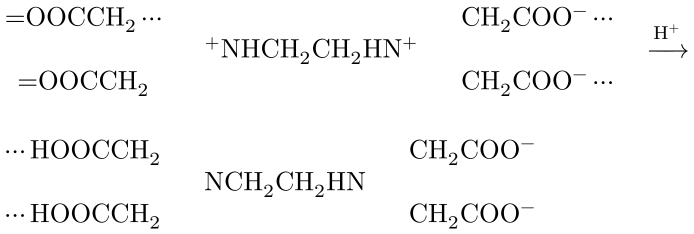
Fig. 2. Change in the refractive index of glasses and crystals along the line *AB* as a function of the ratio NaOH/H_4T.

In the IR spectra of glasses and crystals the most substantial differences are observed in the region 1300–1700 cm^{-1}. Comparatively recently the IR spectra of EDTA anions (H_3T^-, H_2T^{2-}, HT^{3-}, and T^{4-}) in solutions (^{10}–^{12}) were studied, and it was shown that with decreasing pH of the solution (and the transition $T^{4-} \rightarrow HT^{3-} \rightarrow H_2T^{2-}$) there is a decrease in intensity, and then the disappearance, of the peak at 1585 cm^{-1} and the appearance of a peak at 1624 cm^{-1}. If one considers

glasses as supercooled liquids, one might have expected an analogous picture of changes in the IR spectra of the glasses (from the composition $Na[LaT] \cdot 1.2Na_4T \cdot 10H_2O$ to $Na[LaT] \cdot 1.2Na_2T \cdot nH_2O$). However, these frequencies are not observed at all in the glasses, which gives grounds to suppose the presence of interaction between EDTA anions and the ion $[LaT]^-$ in supersaturated solutions and glasses, and the absence there of these anions in the "pure" form. This can hardly be explained by the fact that these frequencies are not resolved against the background of the intense peak at 1600 cm^{-1}, since, for example, in the IR spectrum of the crystalline phase $Na[LaT] \cdot 1.2Na_{1\ 8}H_{2\ 2} \cdot nH_2O$, the frequencies 1600 and 1624 cm^{-1} (characteristic, respectively, of Na[LaT] and Na_2H_2T) are clearly visible, and 1670 cm^{-1} is somewhat less distinct (Fig. 3, spectrum 4). Uncomplexed anions HT^{-3} and T^{-4} can participate (through their $-COO^-$ groups) in binding complex ions $[LaT]^-$ into aggregates of a two- or three-dimensional character. Additional coordination of $-COO^-$ groups is possible through displacement of a water molecule coordinated by the central atom (possibly attached at coordination position 7 (^{13}-^{15})). For complexonates of rare-earth elements, the possibility of increasing the coordination number of the central atom to eight has also been discussed (^{16}). Crystallization of the solution begins after passing the boundary $NaOH/H_4T < 2$ (composition $Na[LaT] \cdot 1.2Na_2 \cdot H_2T \cdot nH_2O$). The literature discusses two possible structures of the H_3T^- ion in solution upon protonation:



$$\begin{array}{lcl} -OOCCH_2 & & CH_2COO^- \\ & {}^{+}NHCH_2CH_2HN^{+} & \\ -OOCCH_2 & & CH_2COO^- \end{array} \xrightarrow{H^+} \begin{array}{lcl} HOOCCH_2 & & CH_2COO^- \\ & {}^{+}NHCH_2CH_2HN^{+} & \\ OOCCH_2 & & CH_2COO^- \end{array} \qquad (11)$$



$$\begin{array}{lcl} =OOCCH_2\cdots & & CH_2COO^-\cdots \\ & {}^{+}NHCH_2CH_2HN^{+} & \\ =OOCCH_2 & & CH_2COO^-\cdots \end{array} \xrightarrow{H^+} \begin{array}{lcl} \cdots HOOCCH_2 & & CH_2COO^- \\ & NCH_2CH_2HN & \\ \cdots HOOCCH_2 & & CH_2COO^- \end{array} \qquad (12)$$

Fig. 3. IR spectra of glasses and the crystalline phase.
1 –glass $Na[LaT] \cdot 1.2Na_4T \cdot 10H_2O$;
2 –glass $Na[LaT] \cdot 1.2Na_3HT \cdot nH_2O$;

3 –glass $Na[LaT] \cdot 1.2Na_2 \cdot H_2T \cdot nH_2O$;
4 –crystals $Na[LaT] \cdot 1.2Na_1\ _8H_2\ _2T \cdot nH_2O$.

The impossibility of forming a stable two- or three-dimensional network in solution (and the appearance of a crystalline phase) at $NaOH/H_4T < 2$ can, it seems to us, be explained by a sharp decrease in the number of reactive $–COO^-$ groups (according to the second scheme) after addition of one proton.

The crystalline phase of composition $Na[LaT] \cdot 1.2Na_1\ _8H_2\ _2T \cdot nH_2O$ has an IR spectrum sharply different from the spectra of the glasses, with frequencies characteristic of the compounds $Na[LaT] \cdot 6H_2O$ and Na_2H_2T, and is evidently a solid solution.

A thermographic study of the glasses and crystals showed that the glasses possess high thermal stability, comparable with the stability of EDTA complexonates, whereas in the crystalline phases the thermal stability decreases, approaching the stability of Na_2H_2T (17). We associate this with the destruction of polymeric chelates after the addition of two protons.

We observed analogous regions of glass formation in systems with complexon IV (H_4R): $Na[LaR]–H_4R–NaOH–H_2O$, and in systems with mixed complexonates: $Na[LaT]–H_4T–Na_2C_2O_4–NaOH–H_2O$, etc.

We found the following regularities of glass formation: in complexonate–complexone (acid)–$NaOH–H_2O$ systems, glass formation is characteristic of the alkaline region ($NaOH / H_4T > 2$). For complexonate–H_2O systems, supersaturated solutions, sometimes turning into glass, are characteristic. In mixed complexonate (acid salt)–$NaOH–H_2O$ systems, glass formation takes place in the acidic region. This confirms our view of polymerization in concentrated solutions through coordination of additional $–COO^-$ groups to the central atom of the complex anion. In the first case these are free groups of the complexone anion (in the acidic region blocked by protons); in the second case, $–COO^-$ groups of one complex ion coordinated by the central atom of another complex ion, with the formation of chains. In the third case, when two strongly bound ligands are located in the inner sphere of the complex, release of a coordination site and polymerization according to the second scheme may occur only when one of the coordinated groups is blocked by a proton.

It is highly significant that the region of glass formation in complexonate–complexone (acid)–$NaOH–H_2O$ systems is at the same time the region of existence of noncrystallizing solutions of the system components and can be used for obtaining stable highly concentrated solutions of these components.

Hydrogen bonds undoubtedly take part in the formation of associates, but their presence cannot be the sole and main explanation of polymerization. First, the region of stable glass formation is associated with a rather narrow interval of the ratio of the component concentrations

$$2.0 < \frac{[-\mathrm{COO}^-]_{\mathrm{free}}}{[\mathrm{LaT}^-]} < 14,$$

whereas the probability of the occurrence of hydrogen bonds is high over a much larger region of the system. Second, after dehydration we obtained anhydrous glasses of compositions $\mathrm{Na[LaT]} \cdot n\mathrm{Na_4T}$ $(0.6 < n < 3.0)$, in which hydrogen bonds must be very weak.

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CITED LITERATURE

[1] D. I. Ryabchikov, V. K. Belyaeva, ZhAKh, 12, 166 (1957).
[2] D. T. Sawyer, P. J. Paulsen, J. Am. Chem. Soc., 80, 1597 (1958).
[3] R. Pfeiffer, W. Offermann, Ber., 75, 1 (1942).
[4] L. I. Martynenko, ZhNKh, 6, 2704 (1961).
[5] L. M. Razbitnaya, Radiokhimiya, 6, 202 (1964).
[6] J. Citron, Anal. chim. acta, 26, 447 (1962).
[7] W. C. E. Higginson, J. Chem. Soc., 1962, 2761.
[8] B. Kirson, J. Citron, Bull. Soc. chim. France, 1959, 365.
[9] N. S. Kurnakov, *Introduction to Physicochemical Analysis*, Publishing House of the Academy of Sciences of the USSR, 1940, p. 223.
[10] K. N. Nakamoto, Y. Morimoto, A. E. Martell, J. Am. Chem. Soc., 85, 309 (1963).
[11] D. T. Sawyer, J. E. Tackett, J. Am. Chem. Soc., 85, 314 (1963).
[12] H. G. Langer, Inorg. Chem., 2, 1080 (1963).
[13] J. L. Hoard, M. Lind, J. V. Silverton, *Advances in the Chemistry of Coordination Compounds*, N. Y., 1961, p. 296.
[14] J. L. Hoard, C. H. L. Kennard, G. S. Smith, Inorg. Chem., 2, 1316 (1963).
[15] M. D. Lind, Diss. Abstr., 23, 1918 (1962).
[16] L. C. Thomson, J. A. Loraas, Inorg. Chem., 2, 89 (1963).
[17] W. W. Wendlandt, Anal. Chem., 32, 848 (1960).

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