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Researching complexation of cyclophosphate–metal systems by physico-chemical methods

We carried out potentiometric and photometric research in the cyclophosphate-modifier system. We set composition of complex compounds formed in systems, show their relative stability. It was given an explanation of the results from the point of view of classical Inorganic Chemistry, theory of hard and soft acids and bases of Pearson and theory of Usanovich.

Key words: synthesis of substances, inorganic, series of solutions, phosphate, solution of sodium, bivalent cation.

Nowadays problem of focused synthesis and control of individual and multicomponent phosphorus-containing systems and polymers composition is very difficult and at the same time unsolved yet. Due to the lack of a fundamental approach to the selection of modifying components for the preparation of compounds with multifunctional properties, the synthesis of multicomponent modified phosphate systems, regardless of their area of use, is carried out by empirical way. In connection with this, it is necessary to have more knowledge on the mechanisms of the hydrolytic decomposition and complexation of polyphosphate — ions with various modifiers.

The purpose of the work is research which enables scientifically justified selection of conditions for the synthesis of compounds and materials based on inorganic phosphorus-containing compounds with multifunctional properties. In this connection, working on the establishment of the composition, properties and determining the conditions of existence of polyphosphate compounds will allow focused search for their practical use, in a particular, preparation of polymer compositions which can be used as highly effective corrosion inhibitors.

Studies were carried out for systems cyclotri- (C3P, $P_3O_9^{3-}$), tetra- (C4P, $P_4O_{12}^{4-}$) and hexaphosphate- (C6P, $P_6O_{18}^{6-}$) with di- (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) and trivalent (Al^{3+}, Cr^{3+}, Fe^{3+}) cations of *p*- and *d*-elements under standard conditions.

Synthesis of research subjects

Synthesis of cyclophosphate was conducted by known methods [1–3].

Identification was performed by IR-spectroscopy by spectrometer UR-20 in the frequency range of 400–3600 cm^{-1} in tablets with KBr. The identification data of the synthesized compounds are in full agreement with the reference data.

Research methods

To obtain the most reliable results, the research was carried out by two independent methods: potentiometric and photometric.

Photometric study of the properties of model systems was carried out using the method of isomolar series and the method of mole ratios.

According to the method of isomolar series solutions was prepared with varying concentrations of the metal C_M and ligand C_L, herewith their total concentration in the solution remained the same, i.e. $C_M + C_L = \text{const} = 0.01$ mol/L. We measured optical densities of the prepared solutions and plotted the graph ofdependence of optical density on the molar proportion of the ligand in solution. Maximum absorption has the solution in which the concentration ratio of the components meets their stoichiometric ratio in the complex. The less stable complex, the more smoothed maximum on the curve [4, 5].

According to the method of mole ratios (saturation method) we prepared a series of solutions with a constant concentration C_M and a variable concentration C_L. We measured the absorbance of the prepared solutions, plotted the graph of dependence of optical density from the molar ratio of the components in solution (saturation curve). The abscissa of the intersection point of the two tangents corresponds to a molar ratio of components in the complex.

Potentiometric study of model systems was carried out using two kinds of titration: titration ofmetal salt solution (0.01 mol/L) with solution of the cyclophosphate (0.01 mol/L); titration of the prepared model system with 0.1 mol/L sodium hydroxide solution [6, 7].

In the titration by the first method the so-called «bath» — specific sites are formed on the potentiometric titration graph, characterizing thecomponents ratio in which stable complexes are formed in the system. Stability of pH over some range of values indicates the formation of a relatively strong compound, the composition of which corresponds to the ratio of the volume of the titrated saltsolution and titrant [8–10].

By the second method the number of available products in the solution of hydrolytic cleavage of initial ortho- and di-form phosphates are determined. Considering that the jump of the titration in such systems is very negligible and to fix it accurately on a regular pH dependence of titrant volume graph with required accuracy is very difficult, we used the method of constructing differentiated titration curve in the coordinates $\Delta pH/\Delta V$ calculating the required data by the formula

$$\frac{\Delta pH}{\Delta V} = \frac{pH_2 - pH_1}{V_2 - V_1}.$$

Results and discussion

Figures 1 and 2 show the graphics results of photometric studies based on the Ni^{2+} – $P_3O_9^{3-}$ model system;

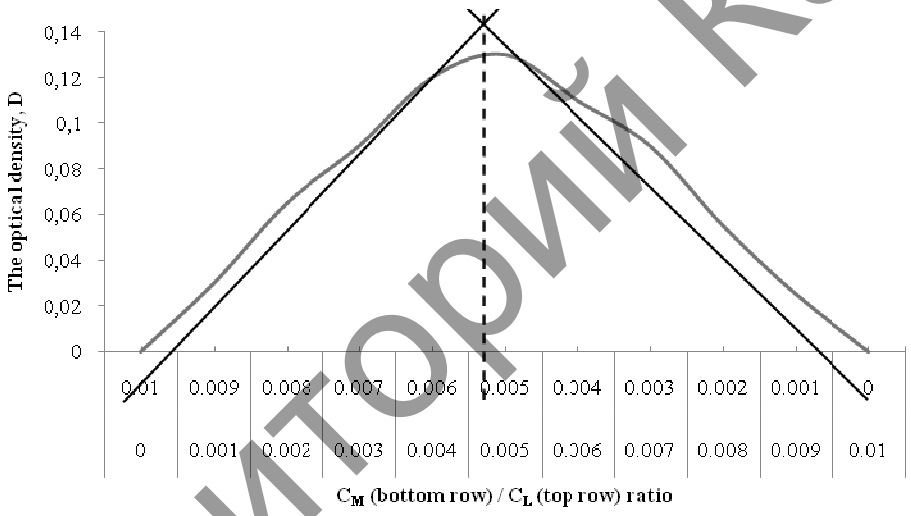

Figure 1. Photometric study of the Ni^{2+} – $P_3O_9^{3-}$ model system by the method of isomolar series

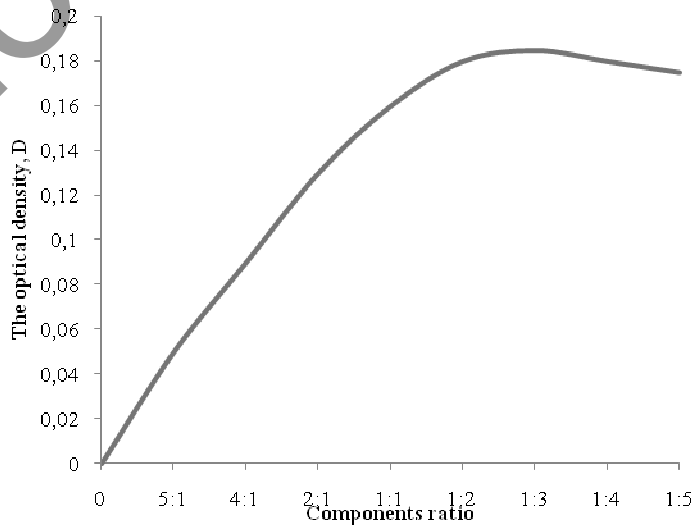

Figure 2. The photometric study of the Ni^{2+} – $P_3O_9^{3-}$model system by the method of molar ratios

Both methods gave similar results — in the system a stable complex with a ratio of 1:1 is formed. An analysis of all systems under study was carried out similarly. By results we obtained the following data about the composition of complex compounds (Tables 1 and 2).

Table 1

Composition of the complex compounds in model systems by the method of isomolar series

	C3P	C4P	C6P
Mn^{2+}	$MnP_3O_9^-$	$MnP_4O_{12}^{2-}$	$MnP_6O_{18}^{4-}$
Fe^{2+}	$FeP_3O_9^-$	$FeP_4O_{12}^{2-}$	$FeP_6O_{18}^{4-}$
Co^{2+}	$CoP_3O_9^-$	$CoP_4O_{12}^{2-}$	$CoP_6O_{18}^{4-}$
Ni^{2+}	$NiP_3O_9^-$	$NiP_4O_{12}^{2-}$	$NiP_6O_{18}^{4-}$
Cu^{2+}	$CuP_3O_9^-$	$CuP_4O_{12}^{2-}$	$CuP_6O_{18}^{4-}$
Zn^{2+}	$ZnP_3O_9^-$	$ZnP_4O_{12}^{2-}$	$ZnP_6O_{18}^{4-}$
Al^{3+}	$AlP_3O_9^0$	$AlP_4O_{12}^-$	$Al_2P_6O_{18}$
Cr^{3+}	$CrP_3O_9^0$	$CrP_4O_{12}^-$	$Cr_2P_6O_{18}$
Fe^{3+}	$FeP_3O_9^0$	$FeP_4O_{12}^-$	$Fe_2P_6O_{18}$

Table 2

Composition of the complex compounds in model systems by the method of mole ratios

	C3P	C4P	C6P
Mn^{2+}	$MnP_3O_9^-$	$MnP_4O_{12}^{2-}$	$MnP_6O_{18}^{4-}$
Fe^{2+}	$FeP_3O_9^-$	$FeP_4O_{12}^{2-}$	$FeP_6O_{18}^{4-}$
Co^{2+}	$CoP_3O_9^-$	$CoP_4O_{12}^{2-}$	$CoP_6O_{18}^{4-}$
Ni^{2+}	$NiP_3O_9^-$	$NiP_4O_{12}^{2-}$	$NiP_6O_{18}^{4-}$
Cu^{2+}	$CuP_3O_9^-$	$CuP_4O_{12}^{2-}$	$CuP_6O_{18}^{4-}$
Zn^{2+}	$ZnP_3O_9^-$	$ZnP_4O_{12}^{2-}$	$ZnP_6O_{18}^{4-}$
Al^{3+}	$AlP_3O_9^0$	$AlP_4O_{12}^-$	$Al_2P_6O_{18}$
Cr^{3+}	$CrP_3O_9^0$	$CrP_4O_{12}^-$	$Cr_2P_6O_{18}$
Fe^{3+}	$FeP_3O_9^0$	$FeP_4O_{12}^-$	$Fe_2P_6O_{18}$

In all systems for cyclo-triphosphate and cyclo-tetraphosphate the formation of most stable complex compounds at a ratio of 1:1is characteristic, and in case for cyclo-hexaphosphate with trivalent cations complexes in a ratio of 2:1 dominate. But in some parts of graphics of dependences there are ill-defined peaks corresponding to complexes of different composition, particularly for systems with cyclo-tetraphosphate.

All systems are additionally subjected to spectrophotometric analysis in the wavelength range of 200–1000 nm determine the presence of interaction of initial components. The absence of absorption in this range indicating that the reacted substances completely changed their composition, and in most cases the region of absorption of formed products, in contrast to the spectra of the initial materials, extend beyond the study area.

The results of potentiometric studies are as follows.

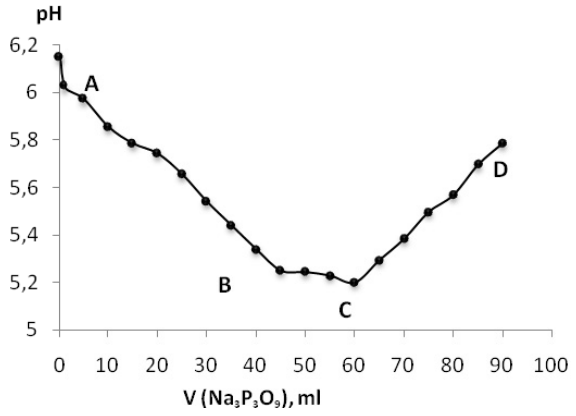

Figure 3. The titration curve of a nickel salt with cyclo-triphosphate solution

Figure 3 shows that a gradual addition of cyclo-triphosphate solution to a solution of a nickel salt initially leads to a decrease in pH. In this case, the solution contains an excess of metal ions which promote the formation of complex compounds in the components ratio closer to 1:1. In aqueous solution of cyclophosphates, alkali metal atoms are replaced by cation of hydrogen, which is subsequently displaced by the cation of metal-modifier, and this is due to decrease in pH in the segment AB. When the ratio is close to 1:1 may form compounds having buffer properties. As a result, the segment BC is formed in the curve. Further increases in the molar ratio of metal and cyclophosphate leads the increase of pH due to excess of phosphate [11, 12].

Similar curves observed for all the systems under study.

In order to determine the qualitative composition obtained cyclophosphate complexes were titrated with sodium hydroxide solution (Fig. 4).

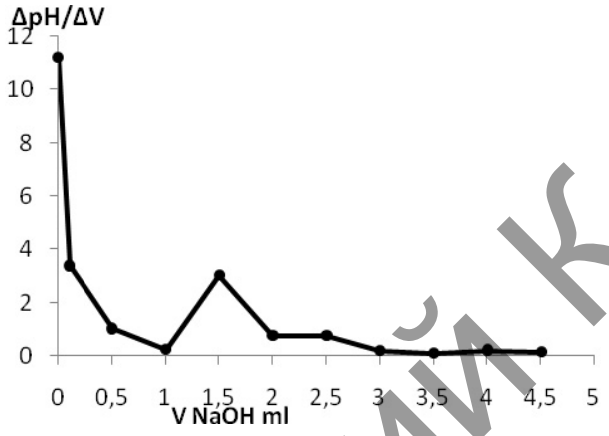

Figure 4. The titration curve of the Ni – $P_3O_9^{3-}$ = 1:1 system with 0.1 mol/L NaOH solution

The presence of a few equivalence points on most titration curves confirms the presence of complexes with a components ratio of 1:1 in systems, but the volume of consumable alkali solution differs, due to various quantitative ratio of products of the hydrolytic cleavage and residue of initial phosphates. The quantitative ratio of products of hydrolytic cleavage depends on the nature of the reacting substances.

The results of potentiometric studies allows to complement data on the composition of model systems obtained by optical methods.

So for systems with cyclo-tetraphosphates and divalent cations in addition to previously identified, according to the results of photometric studies, complexes with composition of 1:1, revealed the formation of weakly stable neutral compounds at components ratio of 2:1. In the case of cyclo-hexaphosphate most stable complexes are formed with trivalent cations at a ratio of 1:1, and at a ratio of 2:1 weakly stable compounds are also formed (Table 3).

Table 3

The most stable forms of the complex compounds in model systems according to the potentiometric studies

	C3P	C4P	C6P
Mn^{2+}	$MnP_3O_9^-$	$MnP_4O_{12}^{2-}Mn_2P_4O_{12}^0$	$MnP_6O_{18}^{4-}$
Fe^{2+}	$FeP_3O_9^-$	$FeP_4O_{12}^{2-}Fe_2P_4O_{12}^0$	$FeP_6O_{18}^{4-}$
Co^{2+}	$CoP_3O_9^-$	$CoP_4O_{12}^{2-}Co_2P_4O_{12}^0$	$CoP_6O_{18}^{4-}$
Ni^{2+}	$NiP_3O_9^-$	$NiP_4O_{12}^{2-}Ni_2P_4O_{12}^0$	$NiP_6O_{18}^{4-}$
Cu^{2+}	$CuP_3O_9^-$	$CuP_4O_{12}^{2-}Cu_2P_4O_{12}^0$	$CuP_6O_{18}^{4-}$
Zn^{2+}	$ZnP_3O_9^-$	$ZnP_4O_{12}^{2-}Zn_2P_4O_{12}^0$	$ZnP_6O_{18}^{4-}$
Al^{3+}	$AlP_3O_9^0$	$AlP_4O_{12}^-$	$AlP_6O_{18}^{3-}$ $Al_2P_6O_{18}$
Cr^{3+}	$CrP_3O_9^0$	$CrP_4O_{12}^-$	$CrP_6O_{18}^{3-}$ $Cr_2P_6O_{18}$
Fe^{3+}	$FeP_3O_9^0$	$FeP_4O_{12}^-$	$FeP_6O_{18}^{3-}$ $Fe_2P_6O_{18}$

Interpretation of the data of potentiometric studies isreduced that regardless of the nature of the cation-modifier for cyclo-triphosphate there is a tendency to form complex compounds with components ratio of

1:1. For cyclo-tetra- and cyclo-hexaphosphateare characterized by two types of relatively stable compounds: the most stable at a components ratio of 1:1 and weakly stable at a components ratio of 2:1.

On the basis of potentiometric data calculated constants for the instability of complex compounds, the dependence of their value on the nature of the cation-modifier and cyclophosphate for 1:1 ratio is illustrated in Figure 5.

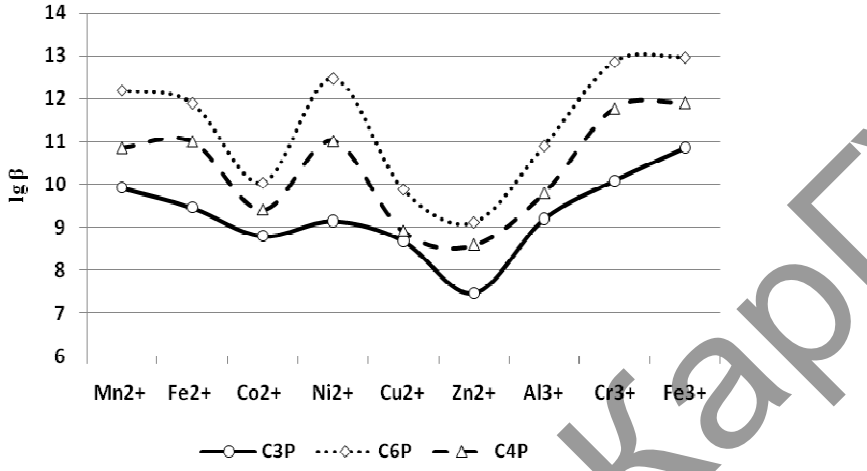

Figure 5. Dependence of the stability constants (lgβ) for complex compounds at a ratio of 1:1, depending on the nature of the cation — modifier and cyclophosphate

A comparison of the stability constants indicates the growing strength of the complex compounds in the transition from cyclo-tri- to cyclo-hexaphosphates, which is consistent with previous data. Among metals the strength of compounds (for all cyclophosphates) increases in the order Zn^{2+} – Cu^{2+} – Co^{2+} – Al^{3+} – Fe^{2+} – Mn^{2+} – Ni^{2+} – Cr^{3+} – Fe^{3+}. This is due to the fact that increasing ionic radius leads to a weakening in the hydrolytic cleavageand an increase in the complexation. However, in the case of zinc, on the other hand, a formation of a less stable complexis seen, that is apparently due to the manifestation of an additional effect of polarization in 18-electron ion.

According to the Usanovich's theory the most acidic function will have zinc ions and they are soft acids according to the HSAB. Therefore, the interaction with a hard base (cyclophosphate-ion) is less preferred and in this case unstable hydrolyzable products are formed. The nature of obtained dependence corresponds to the chemical behavior of elements of the sub-groups.

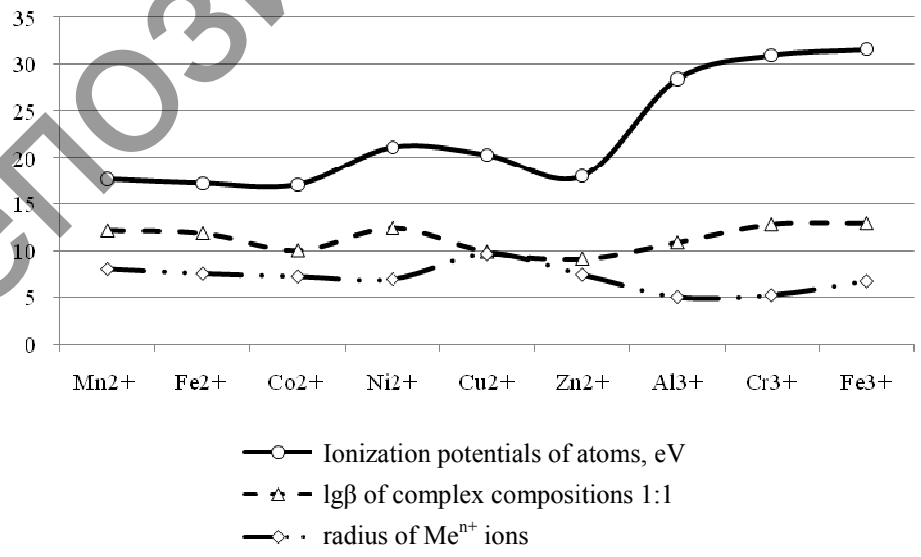

Figure 6. The correlation dependence lgβ of complex compounds on change of the ionization potential and the ionic radii of metal-modifiers

The curves in Figure 6 show a regular change in the stability constants in the range of Zn^{2+} – Cu^{2+} – Co^{2+} – Al^{3+} – Fe^{2+} – Mn^{2+} – Ni^{2+} – Cr^{3+} – Fe^{3+} by increasing the ionization potentials and the corresponding decrease in ionic radii. Such a sequence of changes in the stability constants is in good agreement with the provisions of HSAB theory, Usanovich's and positions of the classical theory of Inorganic Chemistry.

Change in complexing ability of cyclophosphate is associated with the change in nature of the P–O bond, in big cyclesapproachingto the bond character inchained phosphates and removing voltage, existing in small rings. Cyclic phosphate anions withsmall size have a relatively high charges and their metal complexes are much less durable, that is explained by low mobility and difficult accessibility of the functional groups for interaction with cation-modifiers. As a result, bytransition to the big cycles the complexing ability increases dramatically.

Conclusions

By results of the research, the composition of the most stable complex compounds formed in these systems, was set with sufficient accuracy.

The sequence of changes in the stability of cyclophosphate complexes is analogous to the change in the stability of diphosphates in water, which is obviously related to their structure and the prevalence of diphosphate-ion as the main product of the hydrolytic cleavage of the initial compounds. The above range of influence of cation-modifiers is related with change of the second ionization potentials of metals, which affects the reduction of their acidic properties, reduction of compound strength and strengthening the hydrolytic processes. Increasing the strength of complex compounds in the transition from cyclo-tri- to cyclohexaphosphates is related with increasing charge and mobility of the individual fragments of cyclohexaphosphate anion due to removing voltage, whereby the latter becomes more hydrolytically stable.

References

1 *Melnikova R., Pechkov B.B., Dzuba E.D., Malashonok I.E.* Condensed phosphates. — Moscow: Nauka, 1985. — 240 p.

2 *Corbridje D.E.C.* The structural of chemistry of phosphates // Bull. soc. fr. miner. et. cristallog. — 1971. — Vol. 94, No. 1. — P. 271–299.

3 *Zhdanov U.F.* Chemistry and technology of polyformings. — Moscow: Khimiya, 1979. — 240 p.

4 *Lazerov A.B., Kubasova L.B., Chudinova N.N.* Receipts and researches and phosphates of alkaline metals. — 1982. — Vol. .18, No. 9. — P. 127–131.

5 *Kukushkin U.N.* Chemistry of coordinated compounds. — Moscow: Vysshaya shkola, 1985. — 544 p.

6 *André Durif.* The development of cyclophosphate crystal chemistry // Solid State Sciences. — 2005. — Vol. 7, Iss. 6. — P. 760–766.

7 *Pearson R.* Hard and soft acids and grounds // Successes of chemistry. — 1974. — Vol. 15, No. 7. — P. 1259–1271.

8 *Tananayev I.B., Lavrov A.B., Chudinova N.N.* Research of phosphates. — 1988. — Vol. 33, No. 5. — P. 2041–2048.

9 *Kuanysh G.C., Makasheva G.R., Kamalova G.G., Niyazbekova A.B.* Complex formation of salts of some d-elements with diphosphate anion // Bull. of KazNU. — 1999. — No. 13. — P. 71–73.

10 *Narayana N., Maria Rao, Gómez-García R., Kornberg A.* Inorganic Polyphosphate: Essential for Growth and Survival // Annual Review of Biochemistry. — 2009. — Vol. 78. — P. 605–647.

11 *Karapetov M.Kh., Drakin C.I.* General and Inorganic Chemistry. — Moscow: Khimiya, 1981. — 428 p.

12 *Genichiro Kura.* Hydrolysis reaction of inorganic cyclophosphates at various acid strengths // Polyhedron. — 1987. — Vol. 6, Iss. 3. — P. 531–533.

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Циклофосфат металл жүйесіндегі комплекс түзуді физика-химиялық әдіспен зерттеу

Циклофосфат-модификатор жүйесінде потенциометрлік және фотометрлік зерттеу жүргізілді. Кешенді қосылыстардың жүйесінде салыстырмалы тұрақтылық көрсетілді. Берілген көзқарас — классикалық бейорганикалық химияның нәтижесі, қатты және жұмсақ қышқылдың, Пирсонның негізі мен Усановичтың қағидасы бойынша түсіндірілді.

А.Е.Нариманова, А.Б.Ниязбекова, Н.В.Акатьев, Т.А.Шакиров, Н.Х.Аймурзина

Исследование комплексообразования в системах циклофосфат – металл физико-химическими методами

Проведены потенциометрические и фотометрические исследования систем циклофосфат – модификатор. Установлены составы образующихся в системах комплексных соединений, показана их относительная устойчивость. Даны объяснения полученных результатов с точки зрения классической неорганической химии, теории жестких и мягких кислот и оснований Пирсона и теории Усановича.