

Quantum-Chemical Modeling of Equilibrium State of Systems Cyclotri-, Tetra-, Penta- and Hexaphosphates with di- and Trivalent Cations of p- and d-elements

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The thermodynamic properties and equilibrium constants of cyclotri-, tetra-, penta- and hexaphosphates systems with di- and trivalent cations, p- and d-elements for different cyclophosphate / metal molar ratios equal 2:1, 1:1, 1:2 and 1:3 were calculated by using PM3 quantum-chemical semi-empirical method. It was shown that the state of systems equilibrium determines their strength and formation patterns.

Key words: Quantum-chemical calculations, Cyclophosphates, Complexation, Hydrolysis.

Currently the empirical methods are not elaborated as the fundamental approach, to the selection of the modifying components for synthesis of multicomponent, modified polyphosphate systems having multifunctional properties.

The aim of this work is to develop the theoretical methods, based on quantum chemistry calculations, for forecasting the structure and properties of phosphate-modified systems. It is expected that the developed methods will allow selecting the conditions for synthesis of substances and materials, based on inorganic phosphorus-containing compounds, having multifunctional properties.

The calculations will concern the process

of hydrolytic cleavage and complexation of cyclophosphate compounds with modifiers. The obtained data will allow not only for scientific method of the appropriate modifiers selection but also for the optimization of synthesis conditions of above mentioned compounds.

Computational algorithm

In order to determine a composition and possible structures of model systems of cyclotri-, tetra-, penta- and hexaphosphates with divalent (Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) and trivalent (Al^{3+} , Cr^{3+} , Fe^{3+}) metal cations at molar ratios of cyclophosphate / metal = 2:1, 1:1, 1:2 and 1:3 the quantum-chemical calculations were performed.

As a computational method the PM3 semi-empirical method was selected. The method is a variant of the semi-empirical molecular orbitals based Hartree-Fock-Roothaan self-consistent field (HFRSCF) method using valence approximation in order to neglect the diatomic differential overlap. The PM3 method belongs to the family of methods developed by M. Dewar School, such as MNDO

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and AM1 methods¹. The method allows calculating the energy and geometry of molecules containing transition metals¹⁻³.

HFR method has two versions: RHF (Restricted Hartree-Fock) for systems with closed shells (an even number of electrons with zero total spin) and UHF (Unrestricted Hartree-Fock) for systems with odd number of electrons. UHF method requires about twice more computational time in comparison to RHF. For systems with closed shells both methods give identical results.

The procedure of calculation included the construction of the molecular structure, the initial optimization employed the method of molecular mechanics using the conjugate gradient algorithm of Polak-Ribiere, for a given value of the mean square gradient (RMS) 0, 01 kcal / mol. The calculation is continued until the total energy reaches a minimum. The equilibrium geometry obtained in this way is used then for the subsequent optimization of the exact PM3 using the same algorithm to find the molecular structure corresponding to a local energy minimum. The conjugate gradient method, as well as gradient descent method are the first order methods i.e. they use the information only from the first derivatives of the function being minimized. However, it advantageously has a high convergence rate^{4, 5, 6}.

The considered systems can be described in the form of interaction of metal cations with cyclophosphate anion at selected molar ratios.

In quantum-chemical methods the prime target function is always the energy from which other properties may be derived as energy derivatives or energy differences.

In calculations of the considered systems, all cyclophosphate were constructed in the same way - oxygen atoms at the double bond were located on the same side of cyclophosphate ring. Initial cyclophosphate-anions were: cyclotriphosphate-ion - $P_3O_9^{3-}$ (C3P), cyclotetraphosphate-ion - $P_4O_{12}^{4-}$ (C4P), cyclopentaphosphate-ion - $P_5O_{15}^{5-}$ (C5P), cyclohexaphosphate-ion - $P_6O_{18}^{6-}$ (C6P).

The choice of the studied systems was based on the following criteria

a) All chosen systems can be described by the same semi-empirical method what allows to perform the comparative analysis of properties of different molecules⁷.

- b) The chosen cyclophosphates can be easily synthesized in the laboratory by known and good developed methods in sufficient quantities and required purities for subsequent practical study⁸.
- c) The selected compounds easily form complexes and have at least one stable valence state.

It is assumed that at complexation stage, the product of the components interaction of systems is a single complex, composed from phosphate and metal in a proportion equal to the ratio of their stoichiometric coefficients.

For each possible structure (different metal atoms positions) the separate calculation of its enthalpy formation has to be performed. As the most stable structure will be considered the structure having the lowest value of enthalpy.

All calculations were carried out for systems in a vacuum

In the semi-empirical methods the enthalpy of formation under standard conditions ΔH_f^0 is calculated according to the equation:

$$\Delta H_f^0 = \sum_I \Delta H_f^0(I) + \left(E_{tot} - \sum_I E(I) \right) \dots (1)$$

where: $\Delta H_f^0(I)$ and (I) - are the standard heat of formation and the total energy of the I^{th} atom, respectively. The oscillating component of the enthalpy (including the zero-point energy E_{zv}) is not taken into account. This drawback is partially compensated by an appropriate parameterization of the applied computational method.

The standard Gibbs energy is associated with the enthalpy and entropy is given by equation:

$$\Delta_f G^0 = \Delta_f H^0 - T \Delta_f S^0 = - RT \ln K_{eq} \dots (2)$$

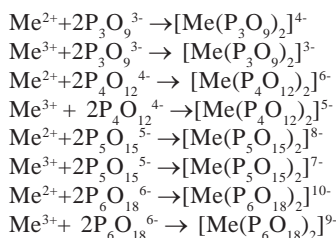
Change in enthalpy in the complexation process in these systems was calculated as the difference between calculated enthalpy of products formation (complex) and reagents (metal cations and cyclophosphate anions):

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reagents}} \dots (3)$$

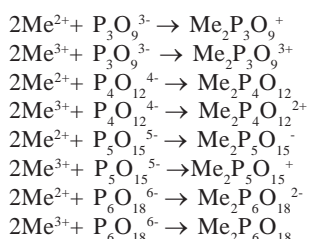
For evaluation and description of the equilibrium state of the studied systems the comparison of calculated energies of hydrolytic release of raw phosphates with the ones modified by complexing was carried out. If the energy of the modified phosphate hydrolytic cleavage at a certain stage is higher than the complexation

The chemical reactions that characterize the systems are as follow

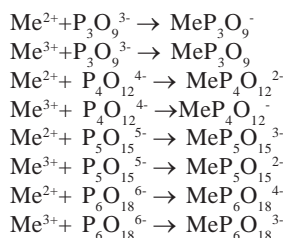
Systems with a ratio of cyclophosphate / metal = 2:1.



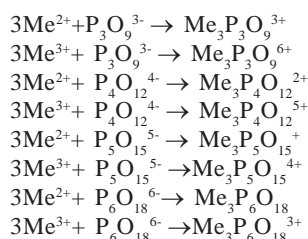
Systems with a ratio of cyclophosphate / metal = 1:2.



Systems with a ratio of cyclophosphate / metal = 1:1.



Systems with a ratio of cyclophosphate / metal = 1:3.



energy, the complexation process dominates in the system, and if lower - hydrolytic cleavage is continued. In the latter case the energy of the cleavage was calculated similarly in then extstage.

According to the Hess's Law⁹, the equilibrium state is described by the total energy of all the successive steps which are required to achieve that equilibrium.

The direction of the hydrolytic cleavage process (the point of attachment of a water molecule and the gap of the P-O) was determined on the basis of calculations of partial charges on atoms. The hydrolytic release of cyclophosphate molecules occurs under the influence of the polar water molecules at the P-O bound where the charge at the phosphorus atom is the biggest and the charge at oxygen atom is the smallest.

In modeling the subsequent structures were built directly from the previous ones, which reduce the errors and makes the virtual models closer to real structures. The structure of final molecule thus strongly depends on the initial boundaries. For example, the structure of the hydrolysis product may be created in two ways:

- 1) by creating the structure from scratch,
- 2) by creating the structure of the initial complex and then adding the H atom and OH group to it at the place of rupture of the

P-O.

Naturally, the second method will be more correct. For example, when calculating the hydrolysis product energy of the complex in the system cyclotriphosphate- $\text{Co}^{2+} = 1:1$ and modeling by the first method, the value of formation enthalpy is -793,31 kJ / mol, and by the second method the value is -865,32 kJ / mol. The higher the number of atoms in a molecule, the more significant the calculated differences. But in all cases the energy of systems calculated by the second method is one order of magnitude lower than the energy of systems calculated with the first method.

The processes direction (from reactants to products) can be meaningfully evaluated with the value of the free Gibbs energy $\Delta_f G^{298.15}$, which should be negative or by value of the equilibrium constant K_{eq} which should be bigger than one. In this case, the concentration of products exceeds the concentration of the reactants and the reaction proceeds mainly towards products and the equilibrium is shifted also to products. If the value K_{eq} is large, the reagents are almost completely converted into products and equilibrium is established at the side of products⁹.

The equilibrium constants were calculated by the change of calculated standard Gibbs energy from equation (2).

RESULTS AND DISCUSSION

The calculated enthalpy of complex compounds formation is shown in Tables 1, 2.

The calculated changes of enthalpy in reactions of complexes formation for the studied systems are shown in Table 3, 4.

Since the modeling was performed for the same conditions, the general dependences of the characteristics for the studied systems are similar. For clarity of the graphical visualization only the average values were used.

Changing of reaction enthalpy of complex compounds formation of the studied systems are illustrated in Fig. 1 as a function of the metal type, cyclophosphate and the components ratio. In a series of divalent cations during the transition from manganese to zinc the strength of complex compounds after some reduction to cobalt increases to maximum value for nickel and then

decreases to a minimum for zinc. In a series of trivalent cations during the transition from aluminum to iron, the stability of resulting complexes increases. The dynamics of such relationships for all the relations in these systems is similar. Calculations show that the most stable complex compounds are formed in systems containing ferric iron, and least stable are systems containing zinc.

When one considers the dynamics stability of cyclophosphates complex (see Fig. 1b) it is revealed that the most stable compounds are formed in the systems with cyclohexaphosphate, and the least stable with cyclotriphosphate. The increase the metal amount in the system during the transition from cyclotri- to cyclohexaphosphate leads to wider variation of the compounds strength. In all the systems with the ratio cyclophosphate / metal = 2:1 the mean value of complexes formation enthalpy is in the range from

Table 1. The calculated enthalpy of formation ($\Delta_f H^{298.15} \text{kJ / mol}$) of cyclophosphate complexes for the ratios of 2:1 and 1:1

| | 2:1 | | | | 1:1 | | | |
|------------------|---------------|------------------|------------------|------------------|---------------|------------------|------------------|------------------|
| | $P_3O_9^{3-}$ | $P_4O_{12}^{4-}$ | $P_5O_{15}^{5-}$ | $P_6O_{18}^{6-}$ | $P_3O_9^{3-}$ | $P_4O_{12}^{4-}$ | $P_5O_{15}^{5-}$ | $P_6O_{18}^{6-}$ |
| Mn ²⁺ | -4854.09 | -4476.41 | -4546.07 | -3896.00 | -3186.07 | -3399.19 | -3896.22 | -4360.37 |
| Fe ²⁺ | -5172.70 | -5316.01 | -5157.72 | -4311.26 | -2521.99 | -3782.92 | -4145.61 | -4614.59 |
| Co ²⁺ | -5197.83 | -5289.54 | -5325.55 | -4735.84 | -2443.54 | -3971.55 | -4573.41 | -4830.74 |
| Ni ²⁺ | -4662.93 | -5082.34 | -4926.82 | -4344.00 | -2613.28 | -3825.94 | -4246.62 | -4613.98 |
| Cu ²⁺ | -4738.63 | -4905.08 | -4730.01 | -4005.15 | -2910.01 | -3420.42 | -4015.37 | -4357.30 |
| Zn ²⁺ | -4476.48 | -4554.57 | -4389.33 | -3637.10 | -3151.91 | -3109.57 | -3591.98 | -3877.85 |
| Al ³⁺ | -5426.53 | -5571.85 | -5958.95 | -5672.74 | -2649.01 | -3899.14 | -4260.43 | -4795.18 |
| Cr ³⁺ | -4993.48 | -5680.10 | -5924.13 | -5523.73 | -2330.37 | -3682.58 | -4517.21 | -5169.56 |
| Fe ³⁺ | -5473.27 | -6182.36 | -6084.23 | -5667.77 | -2306.51 | -4395.39 | -4983.03 | -5391.28 |

Table 2. The calculated enthalpy of formation ($\Delta_f H^{298.15} \text{kJ / mol}$) of cyclophosphate complexes for the ratios of 1:2 and 1:3

| | 2:1 | | | | 1:1 | | | |
|------------------|---------------|------------------|------------------|------------------|---------------|------------------|------------------|------------------|
| | $P_3O_9^{3-}$ | $P_4O_{12}^{4-}$ | $P_5O_{15}^{5-}$ | $P_6O_{18}^{6-}$ | $P_3O_9^{3-}$ | $P_4O_{12}^{4-}$ | $P_5O_{15}^{5-}$ | $P_6O_{18}^{6-}$ |
| Mn ²⁺ | -2613.28 | -3338.37 | -4486.73 | -5480.42 | 642.50 | -1831.15 | -3528.13 | -5425.85 |
| Fe ²⁺ | -2649.01 | -4517.40 | -5862.07 | -7044.26 | 871.42 | -3867.74 | -6415.53 | -8274.32 |
| Co ²⁺ | -3151.91 | -4488.19 | -5916.22 | -6429.88 | 444.98 | -2628.92 | -5218.34 | -6744.49 |
| Ni ²⁺ | -2443.54 | -4167.28 | -5272.45 | -6159.00 | 2195.08 | -381.41 | -4229.79 | -6061.03 |
| Cu ²⁺ | -2330.37 | -3388.43 | -4609.46 | -5110.18 | 1297.30 | -1227.86 | -2529.32 | -5402.34 |
| Zn ²⁺ | -2306.51 | -2767.04 | -3823.13 | -4199.04 | 1119.49 | -754.33 | -2281.54 | -4183.26 |
| Al ³⁺ | -2910.01 | -1911.64 | -4183.03 | -5867.14 | 6084.97 | 2598.86 | 104.66 | -2294.18 |
| Cr ³⁺ | -2521.99 | -1353.08 | -3860.61 | -5621.87 | 5622.86 | 4765.01 | 1966.85 | -1061.28 |
| Fe ³⁺ | -3186.07 | -2997.69 | -5096.23 | -6965.92 | 7057.60 | 1574.42 | -2122.17 | -2858.34 |

-5600 to -6400 kJ/mol. For the ratio cyclophosphate / metal = 1:3, this value is in the range from - 10 000 kJ / mol (for the systems with cyclotriphosphate) to -20000 kJ / mol (for the systems with cyclohexaphosphate).

Experimental data indicate that in the modified phosphate solutions there are two simultaneous competing processes: hydrolytic cleavage and complexation. At the same time complexing cations repeatedly accelerate the process of hydrolytic cleavage of raw phosphates¹⁰.

¹¹. Consequently, the behavior of the systems should be similar.

At the first stage, the system under goes complexation process. Metals contacting the raw phosphate form a complex which is either stored, remaining in a stable condition, or undergoes sequential hydrolytic cleavage process. Thus, depending on the nature of the metal, the system may behave differently, and the depth of hydrolytic cleavage may be different. The equilibrium state of the systems will be achieved when the phosphate

Table 3. Calculated change enthalpy of formation reaction ($\Delta H^{298.15}$ kJ / mol) of cyclophosphate complexes for the ratios of 2:1 and 1:1

| | 2:1 | | | | 1:1 | | | |
|------------------|---|--|--|--|---|--|--|--|
| | P ₃ O ₉ ³⁻ | P ₄ O ₁₂ ⁴⁻ | P ₅ O ₁₅ ⁵⁻ | P ₆ O ₁₈ ⁶⁻ | P ₃ O ₉ ³⁻ | P ₄ O ₁₂ ⁴⁻ | P ₅ O ₁₅ ⁵⁻ | P ₆ O ₁₈ ⁶⁻ |
| Mn ²⁺ | -6115.15 | -5332.39 | -5328.17 | -4848.74 | -5821.83 | -6405.20 | -6865.30 | -7413.88 |
| Fe ²⁺ | -5499.16 | -5237.38 | -5005.22 | -4329.40 | -4922.96 | -5854.33 | -6180.08 | -6733.50 |
| Co ²⁺ | -5320.24 | -5006.86 | -4969.01 | -4549.93 | -5221.81 | -5838.91 | -6403.83 | -6745.60 |
| Ni ²⁺ | -6585.94 | -6600.26 | -6370.87 | -5958.69 | -6314.04 | -7493.89 | -7877.64 | -8329.44 |
| Cu ²⁺ | -4892.55 | -4653.91 | -4404.97 | -3850.74 | -4431.77 | -5319.29 | -5877.30 | -6303.66 |
| Zn ²⁺ | -3354.41 | -3027.41 | -2788.30 | -2206.70 | -3131.93 | -3732.44 | -4177.92 | -4548.23 |
| Al ³⁺ | -6386.01 | -6126.24 | -6439.47 | -6323.89 | -5816.98 | -6603.57 | -6927.92 | -7547.11 |
| Cr ³⁺ | -8821.63 | -9103.16 | -9273.32 | -9043.56 | -8297.62 | -9255.67 | -10053.37 | -10790.16 |
| Fe ³⁺ | -10166.85 | -10470.85 | -10298.85 | -10053.03 | -9827.13 | -10833.91 | -11384.62 | -11877.30 |

Table 4. Calculated change enthalpy of formation reaction ($\Delta H^{298.15}$ kJ/mol) of cyclophosphate complexes for the ratios of 1:2 and 1:3

| | 2:1 | | | | 1:1 | | | |
|------------------|---|--|--|--|---|--|--|--|
| | P ₃ O ₉ ³⁻ | P ₄ O ₁₂ ⁴⁻ | P ₅ O ₁₅ ⁵⁻ | P ₆ O ₁₈ ⁶⁻ | P ₃ O ₉ ³⁻ | P ₄ O ₁₂ ⁴⁻ | P ₅ O ₁₅ ⁵⁻ | P ₆ O ₁₈ ⁶⁻ |
| Mn ²⁺ | -10155.73 | -11500.43 | -12611.85 | -13690.86 | -12878.14 | -15149.25 | -16809.29 | -18792.33 |
| Fe ²⁺ | -9293.72 | -10810.24 | -12117.98 | -13385.49 | -9845.41 | -14382.03 | -16892.88 | -18836.98 |
| Co ²⁺ | -8712.95 | -10372.94 | -11764.04 | -12363.01 | -9659.71 | -12531.06 | -15083.54 | -16695.01 |
| Ni ²⁺ | -11417.41 | -13653.22 | -14721.45 | -15693.32 | -13311.39 | -15685.34 | -19496.78 | -21413.34 |
| Cu ²⁺ | -7644.15 | -9336.19 | -10520.29 | -11106.32 | -8901.90 | -11224.52 | -12489.04 | -15447.38 |
| Zn ²⁺ | -4853.46 | -6162.83 | -7181.99 | -7643.21 | -5251.75 | -6923.03 | -8413.30 | -10400.34 |
| Al ³⁺ | -7394.51 | -9470.53 | -16078.92 | -13474.41 | -6530.92 | -9814.49 | -12271.75 | -18959.21 |
| Cr ³⁺ | -11849.91 | -14649.30 | -21493.83 | -18966.48 | -15599.04 | -16254.35 | -19015.57 | -26332.32 |
| Fe ³⁺ | -15557.86 | -18024.77 | -24460.31 | -22041.38 | -16760.58 | -22041.21 | -25700.87 | -30725.66 |

Table 5. Energy of stepwise hydrolytic cleavage of free cyclophosphate- ions (kJ / mol)

| | I stage | II stage | III stage | IV stage | V stage | VI stage | Complete hydrolysis |
|--|---------|----------|-----------|----------|---------|----------|---------------------|
| P ₃ O ₉ ³⁻ | -155.00 | -468.69 | -236.18 | - | - | - | -859.87 |
| P ₄ O ₁₂ ⁴⁻ | -243.42 | -596.45 | -417.08 | -477.82 | - | - | -1734.77 |
| P ₅ O ₁₅ ⁵⁻ | -372.59 | -1013.25 | -485.97 | -236.61 | -279.14 | - | -2387.57 |
| P ₆ O ₁₈ ⁶⁻ | -545.42 | -1350.82 | -444.83 | -440.32 | -270.09 | -312.69 | -3364.17 |

Table 6. Table of equilibrium states of cyclophosphate - metal systems

| | C3P | C4P | C5P | C6P | C3P | C4P | C5P | C6P | C3P | C4P | C5P | C6P | C3P | C4P | C5P | C6P |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| | 2:1 | | | | 1:1 | | | | 1:2 | | | | 1:3 | | | |
| Mn ²⁺ | | | | | | | | | | | | | | | | |
| Fe ²⁺ | | | | | | | | | | | | | | | | |
| Co ²⁺ | | | | | | | | | | | | | | | | |
| Ni ²⁺ | | | | | | | | | | | | | | | | |
| Cu ²⁺ | | | | | | | | | | | | | | | | |
| Zn ²⁺ | | | | | | | | | | | | | | | | |
| Al ³⁺ | | | | | | | | | | | | | | | | |
| Cr ³⁺ | | | | | | | | | | | | | | | | |
| Fe ³⁺ | | | | | | | | | | | | | | | | |

- the system is stable at the stage of complexation,
- the system is stable at the first stage of the hydrolytic cleavage (disclosure of cyclophosphating),
- the system undergoes the hydrolytic cleavage at 2 or more stages.

complexes hydrolytic cleavage process will stop.

There are some controversial facts in the considered dependence, particularly in the case of cyclophosphate : metal ratio = 2:1, where the calculations of complexation suggest greater stability of cyclotricomplexes in comparison to all others. In the case of the 1:2 ratio the cyclopentaphosphate complexes formation energy is slightly lower than that for hexaphosphate ones. This indicates on the possible instability of some systems and may lead to incomplete complexation stage. To verify these observations, the calculations of equilibrium states of the systems were performed.

Table 5 shows the calculated energy of hydrolytic cleavage of free cyclophosphate ions, separately for each reaction stage. The total energy

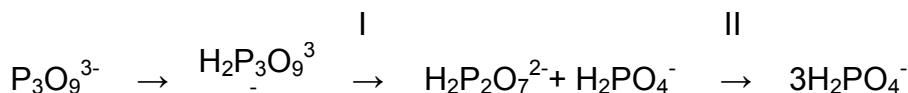
of all stages is the energy of complete hydrolytic cleavage from cyclophosphates to orthophosphates.

Following the algorithm for the systems undergoing the series of hydrolytic cleavage, further calculations of the equilibrium state were carried out. For the equilibrium state of each system the standard thermodynamic parameters: enthalpy (3), entropy, Gibbs energy, and the equilibrium constant (2) were calculated.

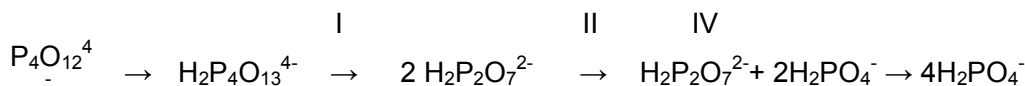
Calculation of stepwise hydrolytic cleavage of cyclophosphate ions

Each stage (indicated by Roman numerals) is the interaction of the reactants with one water molecule resulting the formation of products of hydrolytic cleavage of the scheme “reagents + H₂O → products”:

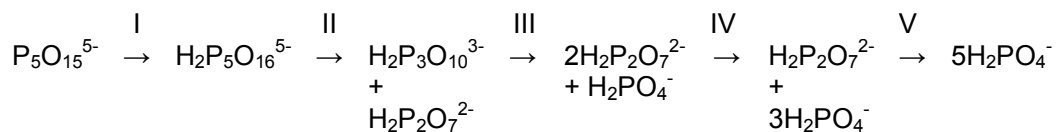
Cyclotriphosphate-ion



Cyclotetraphosphate-ion



Cyclopentaphosphate-ion



Cyclohexaphosphate-ion

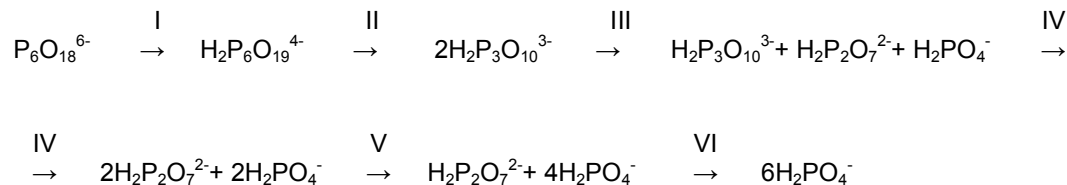


Table 6 summarizes the state of the systems when achieving the equilibrium. It is seen that the influence of the cation nature on the state of the systems is not the same. Most of the systems (91 of 144) remained stable at stage I, and the energy of the equilibrium state corresponds to the energy of complexation reaction. The remaining 53 systems undergo further hydrolytic cleavage process. Most of the systems reached equilibrium in the first stage.

The first stage of the hydrolytic cleavage

is reduced to the opening of the cyclophosphate ring. In the complex compounds, the opening occurs as close as possible to the metal-complexing atoms. Calculations indicate the transfer of the negative charge from the phosphate groups to the metal atoms, but the charge of the metals will still have a positive value (respectively +2 and +3), but in some cases it can become negative.

The Fig. 2b shows the linear dependence of the system stability on the cyclophosphate nature what indicates on the correctness of the

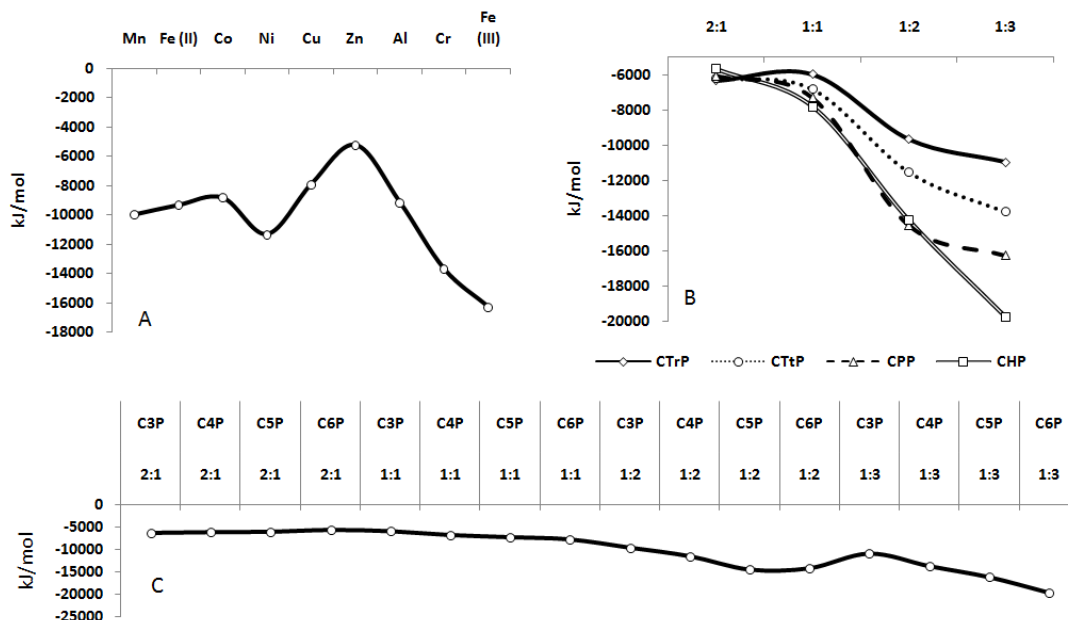


Fig. 1. The enthalpy change in the complexation reaction in the systems cyclophosphate / metal depending on the nature of the metal (A), the nature cyclophosphate (B) and the molar ratios of (C)

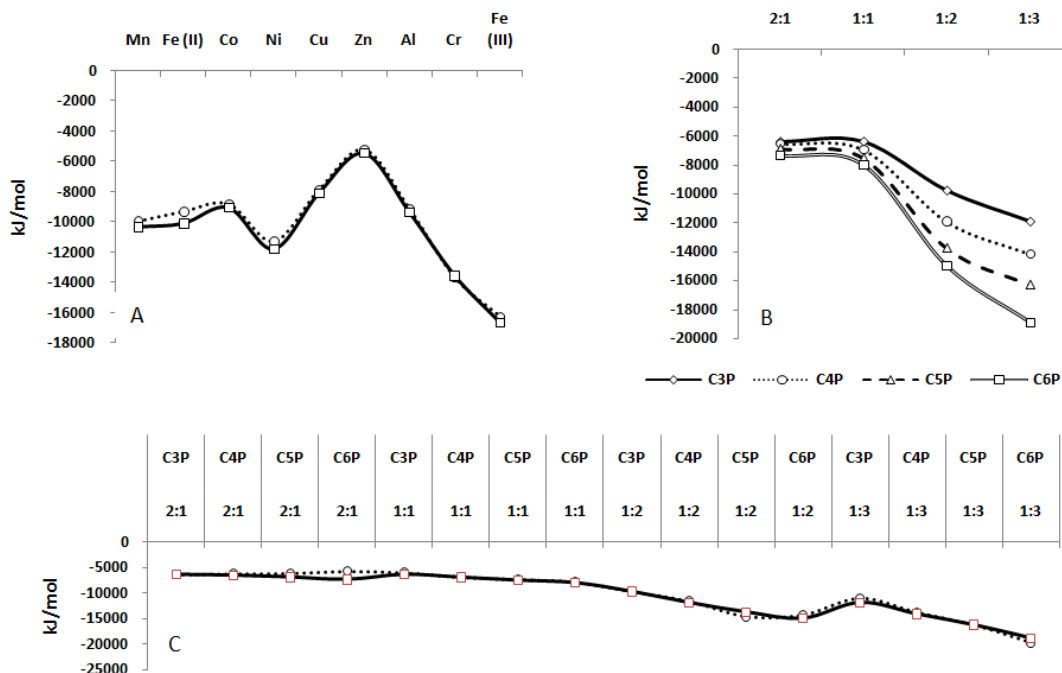


Fig. 2. Enthalpy change on reaching an equilibrium condition in systems cyclophosphate / metal depending on the nature of metal (A), the nature of cyclophosphate(B) and molar ratios (C). For comparison by a dotted line on schedules of an enthalpy change at reaction of a complex formation of Fig. 1A and 1C is designated

applied algorithm used in modeling.

The most unstable relatively to hydrolysis systems were the systems with a cyclophosphate: metal ratio = 2:1, where all the studied metals cause the hydrolysis of the cyclophosphate. The most stable are the systems with the ratio of 1:2 and 1:1 for the cyclohexaphosphate.

CONCLUSIONS

1. The stability of complex compounds (measured with the value of ΔH_{form} , kJ/mol) at all ratios of components increase in the order: $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Al}^{3+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+}$

The most stable are complexes of ferric iron, the most unstable - zinc complexes. The most stable complex is formed in the system cyclohexaphosphate/ Fe(III) = 1:3 characterized by the value of $\Delta H_{\text{form}} = -3072,66$ kJ / mol, the least stable complex is formed in the system cyclohexaphosphate / Zn = 2:1 characterized by the value of $\Delta H_{\text{form}} = -2206,70$ kJ / mol.

2. In the transition from cyclotri- to cyclohexaphosphates the the stability of the formed complexes increases.

3. With the increase of metal concentration in the systems, the stability of formed complexes also increases.

4. For a series of divalent cations the tendency to form complex compounds increases as follows: $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}$,

5. For a series of trivalent cations the tendency to form complex compounds increases as follows: $\text{Al}^{3+} > \text{Cr}^{3+} > \text{Fe}^{3+}$.

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