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CALCULATION OF KINETIC PARAMETERS
OF AMINO-FORMALDEHYDE POLYMERS FORMATION
IN THE PRESENCE OF CALCIUM IONS

В.В. Архипова, Р.В. Смотраєв, О.В. Груздєва. **Розрахунок кінетичних параметрів утворення карбамідоформальдегідних полімерів в присутності йонів кальцію.** Карбонат кальцію — один із широко використовуваних наповнювачів композиційних матеріалів. Сфери його застосування залежать від дисперсного складу, форми частинок та ін. Модифікація карбонату кальцію високомолекулярними полімерами дозволяє в широкому діапазоні змінювати його характеристики і властивості поверхні. Модифікація карбонату кальцію часто проходить з використанням карбамідоформальдегідних полімерів (КФП). ***Мета:*** Метою дослідження є визначення кінетичних характеристик процесу поліконденсації карбамідоформальдегідних полімерів в присутності йонів кальцію. ***Матеріали і методи:*** Механізм поліконденсації КФП складний і залежить від багатьох чинників. Поліконденсація КФП проходила за таких умов: температура — 20, 30, 60 °C; мольне співвідношення карбаміду до формальдегіду — 1:1,25; тривалість поліконденсації — 2 години; масове співвідношення CaCO₃:КФП = 1:1. Процес поліконденсації проводився в розчині хлориду кальцію з pH = 2…5,5. У процесі експерименту визначали концентрацію формальдегіду і метилольних груп хімічним титриметричним методом. ***Результати:*** Показано, що проведення процесу поліконденсації КФП в присутності йонів Ca²⁺ при їх концентрації від 0 до 2,25 моль/л (0…90 г/л) приводить до прискорення процесу при температурі 20 °C більш, ніж в 1,8 разу. Подальше збільшення концентрації Ca²⁺ призводить до зниження швидкості процесу. При температурі 30 °C швидкість практично не змінюється у діапазоні концентрацій Ca²⁺ від 0 до 2,25 моль/л і далі несуттєво знижується. При температурі 60 °C для всього діапазону концентрацій Ca²⁺ спостерігається зменшення швидкості процесу. Вплив Ca²⁺ на процес поліконденсації підтверджує раніше висунуте припущення про утворення слабких зв'язків між КФП і йонами кальцію, які при низьких температурах перешкоджають гідролізу метиленсечовини і руйнуються при підвищенні температури процесу.

Ключові слова: карбонат кальцію, карбамідоформальдегідні полімери, константа швидкості.

V.V. Arhipova, R.V. Smotraiev, O.V. Gruzdeva. **Calculation of kinetic parameters of amino-formaldehyde polymers formation in the presence of calcium ions.** Calcium carbonate is on of widely used fillers of composite materials. The area of its application depend on disperse structure, particle shape and other. The modification of calcium carbonate by high-molecular polymers allows changing its characteristics and surface properties in a wide range. The modification of calcium carbonate often carried out with use of amino-formaldehyde polymers (AFP). ***Aim:*** The aim of this work is to determine the kinetic characteristics of amino-formaldehyde polymers polycondensation process in the presence of calcium ions. ***Materials and Methods:*** The mechanism of AFP polycondensation is complex and depends on various factors. Polycondensation of AFP took place under following conditions: the temperature is 20, 30, 60 °C; the molar ratio of carbamide to formaldehyde is 1:1.25; the polycondensation duration is 2 hours; the mass ratio of CaCO₃:AFP = 1:1. The polycondensation process was carried out in calcium chloride solution with pH=2…5.5. The concentration of formaldehyde and metilol groups determined during the experiment using chemical titrimetric method. ***Results:*** It is shown that polycondensation process of AFP in the presence of Ca²⁺ ions at their concentration from 0 to 2.25 mol/l (0…90 g/l) leads to acceleration of process more than by 1.8 times at temperature of 20 °C. Further increase of Ca²⁺ concentration leads to reduction of process speed. At temperature of 30 °C the speed of process almost does not change in the range of Ca²⁺ concentration from 0 to 2.25 mol/l and further decreases slightly. For all range of Ca²⁺ concentration at temperature of 60 °C the reduction of process speed is observed. Influence of Ca²⁺ on process of polycondensation confirms assumption made earlier of formation of weak bonds between AFP and calcium ions which at low temperatures interfere with hydrolysis of methyleneurea and collapse at increasing of process temperature.

*Keywords*: calcium carbonate, amino-formaldehyde polymers, constant of speed.

Introduction. Calcium carbonate is on of widely used fillers of composite materials. The main characteristics defining possibility of its use as a filler are dispersion and particle shape. Calcium carbonate modification by high-molecular polymers allows changing its characteristics (dispersion, phase structure, particle shape) and properties of surface with the broad range. The widespread amino-formaldehyde polymers (AFP) have been used for modification. Carrying out of polycondensation process and hardening of AFP under certain conditions leads to sludge formation with the developed surface and reactionary and active functional groups on it. Such structure of AFP allows applying

them for coprecipitation with non-organic substances with further use of precipitations in various composition structures.
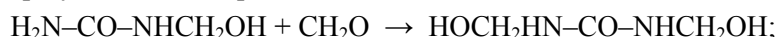
The polycondensation mechanism of AFP is complex and depends on many factors (pH of environment, temperature, concentration of reagents, availability of catalysts and ions of metals or inhibitors) [1…4]. The equation of carbamide reaction with formaldehyde at equimolecular ratio of components, leading to formation of linear structure prepolymers (monomethylol ureas) has the following form:

$$H_2N–CO–NH_2 + CH_2O \rightarrow H_2N–CO–NHCH_2OH.$$
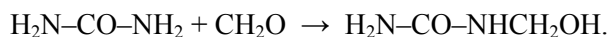
Further polycondensation of monomethylol urea with formation of polimetilenmochevina courses in the following way:

$$nH_2N–CO–NHCH_2OH \rightarrow H[–HN–CO–NHCH_2–]nOH + (n–1)H_2O.$$

Small excess of formaldehyde (25 % of stoichiometry) leads to formation of dimethylol ureas which are also pass polycondensation process:

$$H_2N–CO–NHCH_2OH + CH_2O \rightarrow HOCH_2HN–CO–NHCH_2OH;$$

$$nHOCH_2HN–CO–NH–CH_2OH \rightarrow H[–HOCH_2N–CO–NHCH_2–]nOH+(n–1)H_2O;$$

$$nHOCH_2HN–CO–NH–CH_2OH \rightarrow H[–HOCH_2N–CO–NH–]nOH+(n–1)CH_2O+(n–1)H_2O.$$

Further increase in amount of formaldehyde leads to formation of three- and tetramethylol ureas, but the speed of these products formation is significantly lower than the formation speed of the first two polymers, therefore their influence on polycondensation process is insignificant. The formed polycondensates either turn into carbamide-formaldehyde resins at pH $\geq$ 5, or, at pH $<$ 5, are emitted from solutions in the form of insoluble high-disperse powders (hardening).

The pH value of the reactionary environment significantly influences not only on the type of the formed product, but also influences on the speed of formation and polycondensation of polymers, which has the minimum values in the pH range from 4 to 8 [1]. Considerable decrease of pH leads to sharp reduction of the metilol groups, that are promote binding of inorganic precipitation due to formation of donor-acceptor connection of polymer with cations (calcium ions) or due to physical interaction, and at pH $>$ 5 the hard products are not formed. Therefore, the pH values during the experiments were used in the range of 2…5, that have been recommended for AFP coprecipitations processes with metal hydroxides [5…8].

As it has been established earlier [9, 10], the presence of amino-formaldehyde polymers at solution allows increasing of transformation degree of calcium ions that can demonstrate formation of the weak bonds arising between calcium ions and amino-formaldehyde polymers by electrostatic attraction or on the donor-acceptor mechanism. Availability of such bonds also influences on polycondensation process of AFP, therefore it was necessary to establish the influence of calcium ions on the speed of this process.

The aim of the research is to determine the kinetic characteristics of polycondensation process of amino-formaldehyde polymers in the presence of calcium ions.

Materials and Methods. Polycondensation of AFP took place under following conditions: the temperature is 20, 30, 60 °C; the molar ratio of carbamide to formaldehyde is 1:1.25; the polycondensation duration is 2 hours; the concentration of calcium chloride (considering on calcium ions) – $C_0(Ca^{2+})$ = 0; 22.5; 40; 45; 70; 90 g/l (0; 0.565; 1.0; 1.125; 1.75; 2.25 mol/l); the mass ratio of $CaCO_3$:AFP = 1:1. The polycondensation process was carried out in calcium chloride solution with pH = 2…5.5.

Results. During the polycondensation process rather fast formation of white precipitation is observed (during 2…5 min.) that demonstrates that process of AFP polycondensation and their hardening proceeds in parallel. During the polycondensation process the concentration of free formaldehyde were defined. It characterizing the course of reaction completeness of the methylol ureas and metilol groups formation, characterizing stitching degree at polycondensation in the solution

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containing Ca^{2+} and in control solution without Ca^{2+}. Dependences of the free formaldehyde and metilol groups concentration on polycondensation time at different pH values are presented on Fig. 1.
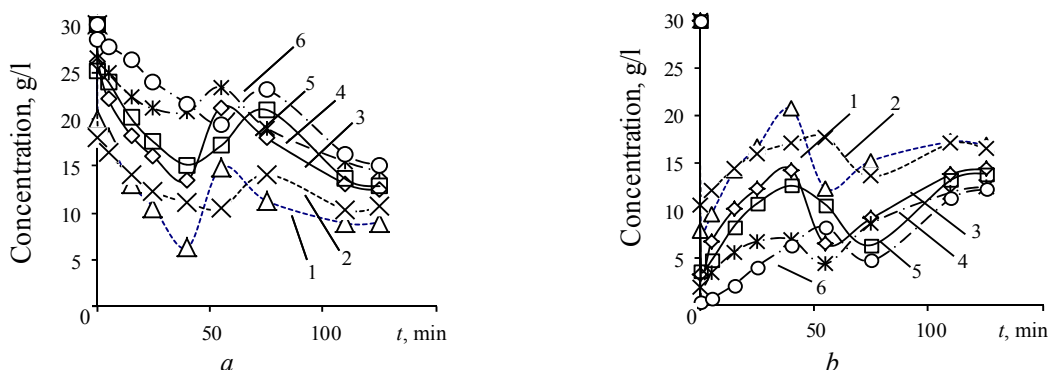

Fig. 1. Dependences of the free formaldehyde (a) and metilol groups (b) concentration on polycondensation time of the AFP: 1 — pH = 2, C(Ca²⁺) = 40 g/l; 2 — pH = 2, C(Ca²⁺) = 0 g/l; 3 — pH = 3.68, C(Ca²⁺) = 40 g/l; 4 — pH = 3.68, C(Ca²⁺) = 0 g/l; 5 — pH = 5.5, C(Ca²⁺) = 40 g/l; 6 — pH = 5.5, C(Ca²⁺) = 0 g/l

In the presence of Ca^2+ cations the acceleration of the first two stages is observed: the maximum concentration of metilol groups (the minimum concentration of free formaldehyde) at the first stage is reached in 40 minutes at presence of Ca^2+ and in 55 minutes without Ca^2+; duration of the second stage – 15 minutes at presence of Ca^2+ and 20 minutes without Ca^2+. The similar accelerating influence of cations on polycondensation process has been described by other researchers [4], however the data about the influence of calcium ions and its mechanism are absent in literature.

Reduction of the solution pH from 5.5 to 2 leads to reduction of free formaldehyde concentration more than by 1.5 times that confirms expediency of the pH value equal 2 accepted earlier for initial stage of AFP obtaining. So, the further calculations were carried out for pH = 2.

The quantitative measure characterizing completeness and speed of all stages of AFP polycondensation (methylol ureas formation, their polycondensation and hardening) is the concentration of the general formaldehyde in solution. Therefore, kinetic parameters of polycondensation process are determined by processing of the general formaldehyde concentration dependences in solution on polycondensation time.

The preliminary analysis of experimental data has shown that the kinetics of the general formaldehyde expenditure in the reactionary environment is described by the kinetic equation of direct reaction of the second order with reverse reaction of the first order [11]:

$$\omega = -\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x) - k_2(c_0 + x) , \qquad (1)$$

where k_1 and k_2 — constants of direct and return reactions speeds;

τ — reaction time;

ω — reaction speed;

a_0, b_0, c_0 — initial concentration of carbamide, formaldehyde and derivatives of methyleneurea, mol/l;

$(a_0 - x)$, $(b_0 - x)$, $(c_0 + x)$ — current concentration of carbamide, formaldehyde and derivatives of methyleneurea;

x — amount of the reacted substance, mol/l.

Equilibrium constant of the process ($K = k_1/k_2$) is:

$$K = \frac{c_0 + \overline{x}}{(a_0 - \overline{x})(b_0 - \overline{x})} , \qquad (2)$$

where $\overline{x}$ — equilibrium value x.

The $\bar{x}$ value is defined by solution of quadratic equation:

$$K(a_0 - \bar{x})(b_0 - \bar{x}) - (c_0 + \bar{x}) = 0,$$ (3)

or

$$K \cdot \bar{x}^2 - \bar{x} \cdot (K \cdot a_0 + K \cdot b_0 + 1) + (K \cdot a_0 \cdot b_0 - c_0) = 0.$$ (4)

Taking into account that $a_0 < b_0$, the gain cannot be more than a_0. Thus, only those values of $\bar{x}$ are physically sensible which are in the range from a_0 to $-c_0$. The values of the trinomial standing, put in the left side of the equation (4), at the ends of this interval, i.e. in points $\bar{x} = a_0$ and $\bar{x} = -c_0$, are equal respectively:

$$F(a_0) = K \cdot a_0^2 - K \cdot a_0^2 - K \cdot a_0 \cdot b_0 - a_0 + K \cdot a_0 \cdot b_0 - c_0 = -a_0 - c_0,$$
$$F(-c_0) = K \cdot c_0^2 + K \cdot a_0 \cdot c_0 + K \cdot c_0 \cdot b_0 + K \cdot a_0 \cdot b_0.$$

If to designate the second root of trinomial as the $\bar{x}'$, then it is possible to write down:

$$F(x) = K(\bar{x} - x)(\bar{x}' - x).$$

At the same time $\bar{x}$ and $\bar{x}'$ are also connected among themselves by:

$$\bar{x} + \bar{x}' = \frac{K \cdot a_0 + K \cdot b_0 + 1}{K}.$$

Then the equation (1) takes the following form:

$$\frac{dx}{dt} = k_1(\bar{x} - x)(\bar{x}' - x).$$ (5)

where $\bar{x}$ — equilibrium value of x, defined from experimental data, at known composition of original and equilibrium stock;

$\bar{x}'$ and k_1 — the sizes, determined of the solution of the differential equation using the formulas given below.

The solution of the differential equation (5) gives the straight line equation in coordinates:

$$\lg\left(\left|\frac{\bar{x}}{\bar{x}'}\right| \cdot \left|\frac{\bar{x} - x}{\bar{x}' - x}\right|\right) = (\bar{x}' - x) \cdot k_1 \cdot \tau.$$

The $k_1(\bar{x}' - x)$ and k_1 are determined by tangent of inclination angle of this straight line to abscissa axis. The equilibrium constant and reverse kinetic constant are defined of the equations (2) and (5).

The example of dependence of the $\lg\left(\dfrac{\bar{x}' - x}{\bar{x} - x}\right)$ on reaction time at concentration of $C_0(Ca^{2+}) = 0{,}565$ mol/l is presented on Fig. 2.
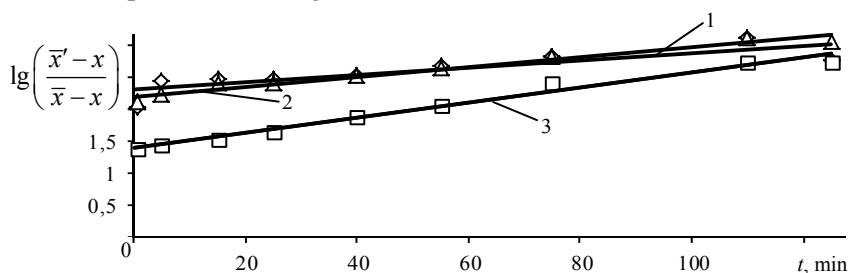

Fig. 2. The dependence of the $\lg\left(\dfrac{\bar{x}' - x}{\bar{x} - x}\right)$ on reaction time at concentration of $C_0(Ca^{2+}) = 0.565$ mol/l

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The examples result for the calculation of the kinetic constants and balance of polycondensation process are presented in table 1. The calculation results of effective kinetic constants of direct and reverse reaction of AFP polycondensation (k_{1ef}, k_{2ef}) for different conditions (initial ion concentrations of Ca^{2+} are 0; 0.565; 1.13; 1.695 respectively; 2.26 mol/l, formaldehyde — 1.0 mol/l, carbamide — 0.8 mol/l; temperature 20, 30, 60 °C; pH=2) are presented in Table 2.

Table 1

Example of calculation of the AFP formation process kinetic parameters

t, °C	$C_0(Ca)$, mol/l	τ, min	K	x'	$\lg\left[\dfrac{\overline{x'}-x}{\overline{x}-x}\right]$	k_{1ef}, $M^{-1}min^{-1}$	k_{2ef}, min^{-1}
						$\times 10^3$	
20	0	0.5	0.189	6.977	1.784	1.049	5.552
		5			2.102		
		15			2.158		
		25			2.189		
		40			2.248		
		55			2.311		
		75			2.299		
		110			2.530		
		125			3.110		
20	0.565	0.5	0.206	6.522	1.726	0.922	4.467
		5			2.062		
		15			2.102		
		25			2.125		
		40			2.125		
		55			2.179		
		75			2.203		
		110			2.479		
		125			2.779		

Table 2

The calculation results of effective kinetic constants of direct and reverse reaction of AFP polycondensation

t, °C	$C_0(Ca)$, mol/l	k_{1ef}, $M^{-1}min^{-1}$	k_{2ef}, min^{-1}
		$\times 10^3$	
20	0	1.049	5.552
	0.565	0.922	4.467
	1.125	0.866	3.676
	1.75	0.703	3.504
	2.25	0.640	3.398
30	0	1.543	6.255
	0.565	1.311	5.880
	1.125	1.240	4.165
	1.75	1.228	3.712
	2.25	1.095	3.679
60	0	4.615	7.093
	0.565	4.260	6.547
	1.125	3.565	5.108
	1.75	3.394	4.830
	2.25	3.105	4.481

Based on the obtained data, the activation energy and preexponential multipliers for direct (E_1) and the reverse (E_2) reaction in solution without presence of Ca^{2+} has been defined:

$$E_1 = 30.2 \text{ kJ/mol}; \quad B_1 = 4.13 \text{ l/(mol·s)};$$
$$E_2 = 4.3 \text{ kJ/mol}; \quad B_2 = 5.55 \cdot 10^{-4} \text{ s}^{-1}.$$

The Arrhenius equations for process of AFP formation in solution without presence of Ca^{2+} takes the following form:

— for direct reaction

$$k_1 = 4.13 \cdot e^{-\frac{30200}{RT}},$$

— for reverse reaction

$$k_2 = 5.55 \cdot 10^{-4} \cdot e^{-\frac{4300}{RT}}.$$

According to the obtained data, the addition to the reactionary Ca^{2+} environment leads to sluggishness of both direct and inverse reactions. The dependences of efficient kinetic constants of a direct and reverse reaction on concentration of Ca^{2+} (Fig. 3) in a general view are described by the following equations:

$$1/k_{1ef} = 1/k_1 - k_1' \cdot C(Ca^{2+}),$$
$$1/k_{2ef} = 1/k_2 - k_2' \cdot C(Ca^{2+}),$$

where k_1' and k_2' — coefficients of proportionalities for a direct and reverse reaction, that are temperature-dependent.

Processing of the dependences presented in Fig. 3 results in the following dependences for coefficients of proportionalities for direct and inverse reactions calculation:

$$k_1' = \frac{1}{2.4 \cdot 10^{-3} - 0.688 \cdot T^{-1}},$$

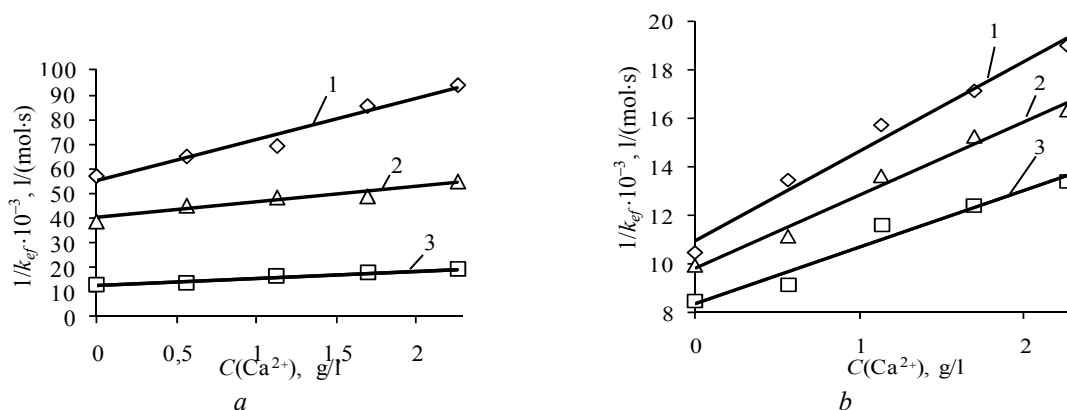$$k_2' = \frac{1}{4 \cdot 10^{-6} \cdot T - 1.92 \cdot 10^{-4}}.$$

Fig. 3. Dependency of the effective constants of direct (a) and reverse (b) reaction speed on concentration of Ca^{2+} at different temperatures: 1 — 20 ℃; 2 — 30℃; 3 — 60 ℃

Thus, the dependences of efficient kinetic constants on concentration of Ca^{2+} and on temperature can be written down in the following form:

$$k_{1ef} = \left(0.242 \cdot \exp\left(\frac{3628}{T} \right) + \left(2.42 \cdot 10^{-3} - \frac{0.688}{T} \right)^{-1} \cdot C(Ca^{2+}) \right)^{-1},$$

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$$k_{2ef} = \left(0.1802 \cdot \exp\left(\frac{515.4}{T}\right) + \left(4 \cdot 10^{-6} \cdot T - 1.92 \cdot 10^{-4}\right)^{-1} \cdot C(\text{Ca}^{2+}) \right)^{-1}.$$

The common speed of AFP formation process in the presence of calcium ions is described by the following equation

$$\omega = \left(0.242 \cdot \exp\left(\frac{3628}{T}\right) + \left(2.42 \cdot 10^{-3} - \frac{0.688}{T}\right)^{-1} \cdot C(\text{Ca}^{2+}) \right)^{-1} (a_0 - x)(b_0 - x) -$$

$$- \left(0.1802 \cdot \exp\left(\frac{515.4}{T}\right) + \left(4 \cdot 10^{-6} \cdot T - 1.92 \cdot 10^{-4}\right)^{-1} \cdot C(\text{Ca}^{2+}) \right)^{-1} (c_0 - x) \tag{6}$$

The relative deviation of the experimental and calculated kinetic constants of reactions does not exceed 5.0 % for a forward reaction, and 11 % for inverse one. I.e. the received results are agree within an experiment error — 3…10 %.

Conclusions. The analysis of equation (6) shows that polycondensation process of AFP in the presence of Ca^{2+} ions at their concentration from 0 to 2.25 mol/l (0…90 g/l) leads to acceleration of process more than by 1.8 times at temperature of 20 °C. Further increase of Ca^{2+} concentration leads to reduction of process speed. At temperature of 30 °C the speed of process almost does not change in the range of Ca^{2+} concentration from 0 to 2.25 mol/l and further decreases slightly. For all range of Ca^{2+} concentration at temperature of 60 °C the reduction of process speed is observed. Influence of Ca^{2+} on process of polycondensation confirms assumption made earlier of formation of weak bonds between AFP and calcium ions which at low temperatures interfere with hydrolysis of methyleneurea and collapse at increasing of process temperature.

Therefore, it is expedient to conduct the process of AFP obtaining at a temperature of 20 °C in solutions with Ca^{2+} concentration within 1…2.25 mol/l (40…90 g/l).

The question of plastics properties studying that use the amino-formaldehyde polymers modified by lime carbonate as an excipient can be considered as a subject of further researches.

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