Physicochemical Particular Qualities of the Crystallization Process of Inorganic Heat-Storage Materials’ Melts

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Abstract

Investigations of the cluster-coagulation model for some inorganic substances and mixtures of sodium thiosulfate with salts of elements (VI) of A, B groups have been carried out. The doping of sodium thiosulfate pentahydrate with sodium selenate, tellurate, molybdate and tungstate has been carried out. The thermodynamic parameters of associate formation processes between sodium thiosulfate and salts formed from oxygen-containing acids of selenium, tellurium, molybdenum and tungsten have been calculated. The amount of heat introduced by the modifier (selenate, tellurate, molybdate and tungstate of sodium) into the total heat-accumulating effect of the mixture Na₂S₂O₃·5H₂O – Na₂XO₄ (X – Se, Te, Mo or W) mixture has been calculated. The number of n-particle clusters and the diameter of clusters that are formed in the melt of the Na₂S₂O₃·5H₂O – Na₂XO₄ mixture have been calculated. It is shown that special effects of systems based on mixtures consisting from sodium thiosulfate pentahydrate and salts of selenium, telluric, molybdenum, tungsten acids could be explained by more excessive tendency of these structures to the hydrate formation, associative stability and polymerization for the reason that rare elements’ ions in anionic form stabilize associates of sodium thiosulfate with water molecules that leads to growth the heat storage capacity.

The scientific and practical significance of this research refers to the probability of prediction physicochemical properties of modified heat-accumulating materials based on the cluster-coagulation model.

1. Introduction

It is known that the development of heat-storage materials on the basis of various chemical compounds involves the preservation of thermal energy through thermochemical reactions, the accumulation of open and latent heat [1] and their use in construction [2]. Widely distributed materials that convert incoming heat as a result of phase transition [3–4], are based on crystal hydrates [5–7], organic compounds [8–10]. However, efficient functioning and operation and selection of heat storage accumulations are possible only if there is information about physical and chemical processes occurring in phase-transition materials.
into account thermodynamic and/or kinetic characteristics of both base and additive. In this regard, the cornerstone in the development of heat-accumulating materials is choice of parametric system; the calculations of heat amount that is accumulated by a mixture of substances will be carried out within this system. The proposed thermodynamic approach allows to adequately evaluate the efficiency of heat-storage materials. This approach based on provisions of the structural organization of components and could be used to identify characteristic features, which determine the heat accumulation possibility by inorganic substances’ mixture.

Therefore, the aim of this research is to evaluate the behavior of some inorganic substances and mixtures of sodium thiosulfate with salts of elements of VI A and B groups’ during crystallization by applying the cluster-coagulation model.

2. Experimental section

2.1. Materials

Sodium thiosulfate pentahydrate (Na$_2$S$_2$O$_3$·5H$_2$O), sodium selenate (Na$_2$SeO$_4$), sodium tellurate (Na$_2$TeO$_4$), sodium molybdate (Na$_2$MoO$_4$), and sodium tungstate (Na$_2$WO$_4$) were used as initial materials for the preparation of heat-storage materials. All the reagents have a purity of reagent grade ($\geq$95%).

2.2. Methods

The preparation of heat-accumulating mixtures. The inorganic mixtures were prepared by mixing sodium thiosulfate pentahydrate and sodium selenate (sodium tellurate) in proportion 50:1 (by weight), weight of sodium thiosulfate is 5 g, based on weight of sodium selenate (tellurate, molybdate, tungstate) additives was calculated. After mixing, the mixtures were heated to a temperature at which solid phase dissolution in the crystallization water was observed. The melting – crystallization process was controlled by a visual-thermal method by measuring the thermo-EMF using a chromel-alumel thermocouple.

2.2.1. The method of thermal analysis

The temperature has been measured using a chromel-aluminum thermocouple of 0.2 mm thick, the junction of which has been immersed into the sample. The error in temperature measurement was 0.5 K, the temperature has been controlled by an electronic voltmeter V7-78 2.

2.2.2. Determination of electrical conductivity of the melts

Conductometric studies were carried out in a 50 ml thermostated vessel. The electrical conductivity was measured on OK-102 conductivity meter.

The pair of platinum plates with area of 1 cm$^2$ were used as the working electrode. To calculate the electrical conductivity from S/cm to Ohm/cm, the instrument constant was determined by measuring the value of $\chi$ in 0.001 M solution of potassium chloride at standard temperature [11]. Melt density was determined by picnometry [12].

Based on the electrical conductivity of melts consisting from sodium thiosulfate crystalhydrate and inorganic additives at different temperatures, the activity and activity coefficients’ values were calculated.

3. Results and discussion

3.1. Thermodynamic properties of heat-accumulating materials

The previous investigations [13–14] demonstrated that the incorporation of rare metal’s ion into crystalline mixtures with abilities of heat accumulation can make an additional positive effect on heat storage. In addition, it was reported about supercooling effect of tin and bismuth was determined using the calculations of the critical sizes of crystal nuclei and uncrystallized clusters.

The method of thermal analysis (the cyclic thermal analysis) allows to reliably determine the value of $\Delta T^*$. According to the cluster-coagulation model [15], the whole crystallization process occurs in three stages, which is clearly confirmed by Fig. 1.

The accumulation of crystals nucleus of various sizes is observed at the first stage that is the cooling process from melting point $T_1$ (point $b$) to temperature $T_{\text{min}}$ (point $c$) during the incubation period of time $\tau_c$ in the supercooled melt. The melt begins to crystallize when metastability is attained the lower boundary of during cooling (point $c$ at temperature $T_{\text{min}}$). At this takes place the temperature rises rapidly from point $c$ to point $d$ during time $\tau_d$. It is likely that by accumulating to critical concentrations in some part of the sample, these particles can coagulate with each other to produce the sufficient amount of heat. In result of this the primary volume of solid phase forms, which is growing at the sacrifice of isothermal re-crystallization of remaining melt during time $\tau_3$ by adding the secondary nucleus and etc. to the increasing front of crystal-
lization centers. The above-enumerated features in the behavior of substances during cooling and crystal formation processes including the stage of explosive crystallization were demonstrated in [16] by the case of water crystallization with supercooling. Taking into consideration that water is a solvent for investigating systems, the effect of explosive crystallization should cover aqueous solutions, but to a lesser degree.

In this way, the prepositions of cluster-coagulation theory are fully confirmed experimentally for the simple substances of iron and bismuth; the estimation of applicability of this theory to the inorganic salts’ crystallization is of interest, for example of sodium thiosulfate modified by salts of VI group elements. For this purpose, the heating-cooling curves (Figs. 2–5) of mixtures of sodium thiosulfate pentahydrate – sodium salts of rare elements have been obtained.

The data shown in Figs. 2–5 shows that heating the mixture above the melting point leads to a clear fracture on the curve 1 for the mixture with sodium tellurate, which disappears when mixtures of sodium selenate and sodium tungstate are melting; whereas the change in the course of the heating process of the mixture is observed in case of the
melt consisting from crystalline hydrate and sodium molybdate. These features have an impact on the cooling process in general and on the transition from crystallization process to cooling of the solid mixed melt. Therefore, the temperature coefficients of the heat capacity for selenate, tellurate, tungstate and molybdate of sodium in the range 298 K – $T_m$ have been determined to establish the effect of additives on the crystallization process by Landiya method [17] (Table 1).

Further the melting temperatures of mixture and the specific melting heat of mixtures of sodium thiosulfate pentahydrate with selenate, tellurate, tungstate, molybdenum of sodium have been calculated based on the kinetic cooling curves (Table 2).

Since all the additives differ from the basic salt only by anion, the main influence on the heat-accumulating characteristics of the mixtures will be due to the strength of hydrogen bonds with tetrahedral anions of (VI) group elements [18–19]. According to the above data, the maximum heat emission for the mixture of pentahydrate of sodium thiosulfate – sodium molybdate is due to the formation of solvate separated ionic pairs, which strengthens the structure of the melt of sodium thiosulfate hydrate.

The change in the specific melting heat of the mixture with an addition of sodium tellurate is that oxoanion binds the solvent molecules and thiosulfate ions into more durable complexes, which requires energy consumptions.

In the transition to selenate ions, the hydration heat increases that leads to reduction of heat-accumulating effect. In the case of sodium tungstate, oxoanion forms its own hydrate, which melts at a higher temperature than sodium thiosulfate so the specific melting heat is reduced. Earlier, the electrical conductivity of mixtures of sodium thiosulfate pentahydrate with sodium selenate [20–21], sodium tellurate [22] sodium tungstate and molybdate [23] had determined. Calculation results of the electrochemical contribution in the heat accumulation by mixtures based on sodium thiosulfate pentahydrate are provided in Tables 3–5.

### Table 1
The temperature coefficients of the heat capacity of the sodium salts

| Compound     | $C_p$, Cal/mole·K | $a$ | $b$·10$^3$ | $c$·10$^5$ | 298 – $T_m$ |
|--------------|-------------------|-----|------------|------------|-------------|
| Na$_2$SeO$_4$ | 35.60             | 5.33| 0.35       | 298–1003 K |
| Na$_2$TeO$_4$ | 36.04             | 4.84| 0.37       | 298–1009 K |
| Na$_2$MoO$_4$ | 35.73             | 5.20| 0.40       | 298–960 K  |
| Na$_2$WO$_4$  | 35.63             | 5.28| 0.39       | 298–969 K  |

### Table 2
The thermodynamic parameters of the melting process of Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$XO$_4$ mixtures

| Mixture           | $T_m$, K | $C_p$(s), J/kg·K | $C_p$(sol), J/kg·K | $\lambda$, kJ/kg | $\rho$, g/cm$^3$ | $V_M$, cm$^3$/mole |
|-------------------|---------|------------------|--------------------|------------------|-----------------|------------------|
| Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$SeO$_4$ | 314     | 833.19           | 1436.34            | 31.47            | 2.7198          | 90.65            |
| Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$TeO$_4$ | 311     | 667.48           | 1430.63            | 69.62            | 1.7405          | 142.33           |
| Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$WO$_4$  | 323     | 537.46           | 1432.98            | 12.12            | 3.8279          | 65.03            |
| Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$MoO$_4$ | 309     | 766.04           | 1432.75            | 97.78            | 5.2364          | 47.14            |

### Table 3
The thermodynamic parameters of the heat storage process with a mixture of sodium thiosulfate pentahydrate – sodium selenite

| T, K | 298 | 338 | 343 | 348 | 353 |
|------|-----|-----|-----|-----|-----|
| $lna_i$ | -5.23 | -4.89 | -4.90 | -4.90 | -4.87 |
| $\overline{T_{\Delta \mu}}$, * kJ·mole$^{-1}$ | 4.13 | 9.77·10$^{-1}$ | 5.84·10$^{-1}$ | 1.90·10$^{-1}$ | -2.04·10$^{-1}$ |
| $\Delta \mu$, kJ·mole$^{-1}$ | 12.97 | 13.74 | 13.97 | 14.181 | 14.38 |

Note: * – The heat content and other thermodynamic values are given to the value of kJ· kg$^{-1}$ of the mixture.
It is shown that the heat content of the mixture decreases with increased temperature, and the heat accumulation process are intensified only the mixture on being heated up to 353 K.

A rising of temperature leads to an increase in the number of interactions between water molecules and a decrease in the proportion of tetrahedrally coordinated solvent molecules. The process of ion association in systems is enhanced on heating [24]. It is also known that the first sphere of metal and anion ions is completely filled with wa-
ter molecules in the equilibrium high-water crys-
talline hydrates. Therefore, sharp differences in
the electrical conductivity of the mixture in infinite dilution and experimental data are associated with
the formation of complex ion-aqueous rather than ion

Thus, the presence of local stable areas with
high charge density is the optimal conditions for
achieving the maximum heat-accumulating effect
from the kinetic positions, and the high activity
of the components of the additive forming com-
plexes due to the energy of hydration, ion-dipole
interaction with solvent molecules from the ther-
modynamic ones. The transition temperature to the
active state is 353 K.

In this case, adding the sodium tellurate in pro-
portion of 1:50 to the base salt leads to increase
the heat content and heat capacity of mixture. It is
shown that the system still emits heat into the envi-
ronment due to the decomposition of the salt asso-
ciates and the additive with the solvent during the
heating up to melting point (51–55 °C). However,
the system passes to the heat storage regime, i.e. the
heat content changes sign from negative to positive
at the temperature 348 K, in so doing the endother-
ic effect increases with increased temperature.

According to the calculations, this mixture is
characterized by a high heat capacity (2400 J/mole
K), therefore the system accumulates the maximum
amount of heat on being heated up to 353 K, that
is emits to the environment during the subsequent
cooling. The calculations showed that the mixture
emits 88 kJ/kg of heat into the environment with
decreased temperature from 353 to 298 K, and this
amount of heat is more than heat determined with
a thermocouple experimentally.

Probably, there is an error in result of not taking
account into the loss of heat or changes in thermal
conductivity of glass and air. The contribution of
tellurate ion to the heat content of the mixture was
also calculated; it was shown that the presence of a
50-fold excess of basic salt contributes to the for-
mation of the most thermodynamically beneficial
structure, in which tellurate ions are binding sites
for solvent molecules (so-called associate sites).

On the other hand, the chemical potential in-
creases on being heated (the positive values ac-
cept). As a result of the studies, optimal conditions
have been found: heating up to 348 K, the stabiliz-
ing effect of tellurate ion on the associates of sodi-
um thiosulfate with water molecules, which togeth-
er allows to accumulate the energy coming to the
system, followed by its emission during cooling.

### Table 4

| T, K   | 298  | 338  | 343  | 348  | 353  |
|--------|------|------|------|------|------|
| lna,   | -2.00| -5.13| -5.17| -5.18| -5.09|
| $\bar{T}_2$,* kJ·mole$^{-1}$ | -40.72| -5.62| -1.24| 3.14 | 7.53 |
| $\Delta\mu$, kJ·mole$^{-1}$   | 4.97  | 14.41| 14.74| 14.97| 15.17|

Note: * – The heat content and other thermodynamic values are given to the value of kJ · kg$^{-1}$ of the mixture

### Table 5

| T, K   | 298  | 338  | 343  | 348  | 353  |
|--------|------|------|------|------|------|
| lna,   | -5.49| -5.09| -5.11| -5.14| -5.18|
| $\bar{T}_2$,* kJ·mole$^{-1}$ | 6.60 | -0.72| -1.64| -2.55| -3.47|
| $\Delta\mu$, kJ·mole$^{-1}$   | 13.61| 14.31| 14.57| 14.88| 15.00|

Note: * – The heat content and other thermodynamic values are given to the value of kJ · kg$^{-1}$ of the mixture
It is shown that the more the activity or the chemical potential of the electrolyte changes with increasing temperature, the higher the amount of accumulated heat due to associative formation. Thus, the heat accumulation process in crystalline hydrate melts is directly proportional to the activity and chemical potential of the additive component (sodium molybdate).

According to the cluster-coagulation model [16] in the systems which melt without over cooling, the clusters are primary particles that can cause crystallization. Therefore, the average number of particles in the cluster for mixtures of Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$TeO$_4$, Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$MoO$_4$ (Fig. 6), Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$SeO$_4$, Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$WO$_4$ (Fig. 7), the proportion of crystal mobility particles $P_{crm,m}$ (Table 6) have been calculated according to the theory of randomized particles [25], allowing to estimate the stability of clusters in a wide range of temperatures from $T_0$ to $T_{boil}$ ($T_0 = 273$ K, $T_{boil} = 373$ K are respectively for crystalline hydrates).

Fig. 6. The dependence of average number of particles in the cluster on the melting temperature of Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$XO$_4$ mixtures (X – Te, Mo).

Fig. 7. The dependence of average number of particles in the cluster on the melting temperature of Na$_2$S$_2$O$_3$·5H$_2$O-Na$_2$XO$_4$ mixtures (X – Se, W).

It is shown that the temperature has the maximum effect on the particles’ number in the cluster for sodium molybdenum, and the minimum – for sodium tungstate. This fact indicates the predominant role of ion mobility in the melt, and hence the electrostatic interactions between the additive oxoanions and solvent molecules.

Moreover, the cluster diameter, number of particles and number of n-partial clusters accounted for one mole of substance have been calculated based on the values of the average integral number of particles in the cluster.

The Table 6 shows that the largest cluster is formed in the presence of sodium molybdenum; the minimum size corresponds to the cluster, which had formed in a mixture of sodium thiosulfate pentahydrate – sodium tungstate. However, share of large clusters is one thousandth of a percent, and the small ones is 5%, which confirms the previously proposed assumption about the formation of solvately separated ionic pairs for molybdenum ions and the formation of thermally stable hydrate of tungstate ion.

Further the volume component of electrostatic Gibbs energy of the cluster formation has been calculated based on the results of density measurements (Table 2) and calculations of changes in the chemical potential of the ionic associates’ formation process in mixtures (Table 6). As it can be seen from Table 6, the contribution to the Gibbs energy is determined by the change in the hydration heat of anion.

The analysis of the curves given in Figs. 1 and 2 showed that the optimum temperature of mixture needed for cluster formation has been found in the region of the limited melting point and boiling point of the mixture. On the other hand, according to the cluster-coagulation model [11], the region of cluster appearance is above the melting temperature and is characterized by melt overheating.

Therefore, the optimal temperature in this case is the maximum temperature at which the crystal structure of the melt is preserved due to the appearance of clusters, and the increase relative to $T_m$ characterizes the melt overheating (Table 6).

Thus, the minimum possible overheating of the mixed melt containing sodium molybdenium is associated with both high mobility of molybdenum ions and low stability of the formed clusters, while the maximum temperature increment for selenite ion is due to the high stability of the clusters and the minimum heat of selenate ion’s formation in the solution.
4. Conclusions

The analysis of the thermal effects that characterize the crystallization of supercooled melts based on the cluster-coagulation model has been carried out. The thermodynamic and electrochemical confirmations of heat accumulation for mixed melts of sodium thiosulfate pentahydrate with selenate, tellurate, molybdate and tungstate of sodium have been found. It is shown that the process of heat accumulation is intensified only when the mixture is on being heated up to 353 K (sodium selenate). The optimal conditions heating to T = 348 K (sodium tellurate) have been found. The stabilizing effect of rare elements ions in anionic form on the associates of sodium thiosulfate with water molecules has been established. Both of them allow accumulating the energy coming to the system, followed by its emission during cooling. The characteristics of the cluster phase during the melting of mixtures of sodium thiosulfate crystalohydrate and of rare elements’ salts have been calculated.

The impact of the nature of selenite-, tellurate-, tungstate- and molybdate-ions on the size of formed cluster has been established. It was found that the optimal temperature not only limits the effective reduction of cluster size on heating, but also is the upper limit of the existence of clusters capable of crystallization.

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