EVALUATION OF THE SODIUM SELENITE AND TELLURATE TO THE THERMODYNAMICS OF HEAT ACCUMULATION BY COMPOSITES BASED ON SODIUM THIOSULPHATE

Abstract: The main category of materials wear in the process of transport, residential premises operation is a temperature difference between external and internal, a high gradient and cyclic changes in the temperature regime lead to changes in the materials structure and an increase in energy consumption.

Therefore, an urgent problem along with the development of heat-storage materials which make it possible to reduce significantly the heat loss to the environment is the matrix modification through the introduction of various additives. The aim of this investigation is the establishing of adding sodium tellurate and sodium selenate to sodium thiosulfate pentahydrate influence on the heat-storage properties of the obtained mixtures. The behavior of sodium selenate and sodium tellurate in the composition of the mixture with sodium thiosulfate crystalline hydrate was studied by the conductivity method. The changes in the activity coefficients of sodium selenate, the contribution of sodium selenate to the heat content of the mixture with sodium thiosulfate pentahydrate were calculated. Also, the changes in the activity coefficients and association degrees of sodium tellurate - sodium thiosulfate pentahydrate mixtures (1:50) were calculated, according to which the complex formation process is exothermic, heat storage process is electrostatic in nature. Consequently, the stability of the associates is decreased with increasing temperature. It was also found that the mixture cooling to T=298 K releases into the environment up to 100 kJ/kg of heat. The temperature of transition to the active state is 353 K. As a result of the studies, optimal warming temperature T=348 K, stabilizing effect of tellurate ion on sodium thiosulfate with water molecules associates were found, which together allows the energy coming to the system accumulation, its release during cooling with subsequent.

Key words: sodium thiosulfate pentahydrate, sodium selenate, sodium tellurate, activity coefficients, heat content, crystalline hydrate melt, electrical conductivity.

Introduction
The increase in energy consumption stimulates the demand for materials possessing not only high heat of combustion, but also capable of accumulating heat as a result of various processes. In this regard, 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 operation and operation and selection of heat storage accumulations is possible only if there is information about physical and chemical processes occurring in phase-transition materials. The final stage, in this case, is the creation of a model for changing the properties of materials in the process of heat accumulation [11], with changes in the physicochemical properties of the material being the basis of any model when the heat capacity and composition are varied [7]. Therefore, the control of the change in properties is actual in the creation of models of heat accumulation [12]. In connection with this, the goal of the work is to establish the behavioral features of sodium selenate and tellurate when used as additives in the development of heat-storage materials.
Methods
Materials. Sodium thiosulfate pentahydrate (Na2S2O3·5H2O), sodium selenate (Na2SeO4) (pure for analysis), sodium tellurate (Na2TeO4), chem.pure, were used as starting materials for the preparation of heat-storage materials.

Preparation of mixtures with heat-accumulating properties. Inorganic mixtures were prepared by mixing sodium thiosulfate pentahydrate and sodium selenate (sodium tellurate) in various proportions by weight (50: 1), the mass of sodium thiosulfate 5 g, from which the mass of additives of sodium selenate (tellurate) was calculated. After mixing, the mixtures were heated to a temperature at which dissolution of the solid phase in the crystallization water was observed.

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

The working electrode was made from a pair of platinum plates with an area of 1 cm2. To calculate the electrical conductivity from Sim/cm to Om/cm, the instrument constant was determined by measuring the value of \(\chi\) in 0.001 M KCl at standard temperature [13].

Calculation of the kinetic characteristics of electrical conductivity. To calculate the kinetic characteristics, the Arrhenius equation was used, in which the rate constant was replaced by the specific electrical conductivity.

The activation energy of electrical conductivity was calculated graphically according to the equation:

\[
\lg \chi = \lg A_0 - \frac{E_a}{2.303RT}
\]  

(1)

Calculation of kinetic characteristics was carried out according to the formulas [14].

\[
\Delta H^\circ = E_a - 2RT
\]  

(2)

Then the value of \(\Delta S^\circ\) was found from the equation:

\[
\Delta S^\circ = R \left[ 2.303 \lg A_0 - 2.303 \left( \frac{kT}{h} \right) - 1 \right]
\]  

(3)

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]  

(4)

Results and Discussion
Earlier, the electrical conductivity of mixtures of sodium thiosulfate pentahydrate with sodium selenate [15-16] and sodium tellurate [17] of different composition (1:10, 1:25, 1:50) was determined. The energy characteristics of electrical conductivity are calculated. It is shown that the main criterion for the choice of heat-accumulating compositions is the thermodynamic stability of the mixture or formed complexes during the interaction of the components of the mixture, which is characterized by the chemical potential, the activity of the substances and the activity coefficients. The results are given for a 1:50 mixture (Table 1).

### Table 1 - The contribution of sodium selenate to the thermodynamic characteristics of the heat storage process

<table>
<thead>
<tr>
<th>T, K</th>
<th>(lna_t)</th>
<th>298</th>
<th>338</th>
<th>343</th>
<th>348</th>
<th>353</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a), kJ·mole(^{-1})</td>
<td>2.27·10(^{-1})</td>
<td>1.36·10(^{-3})</td>
<td>4.53·10(^{-2})</td>
<td>-4.54·10(^{-2})</td>
<td>-1.36·10(^{-2})</td>
<td></td>
</tr>
<tr>
<td>(\Delta \mu_a), kJ·mole(^{-1})</td>
<td>5.24</td>
<td>6.02</td>
<td>6.14</td>
<td>6.25</td>
<td>6.32</td>
<td></td>
</tr>
<tr>
<td>(\Delta S), J·mole(^{-1})·K(^{-1})</td>
<td>-15.60</td>
<td>-16.72</td>
<td>-17.53</td>
<td>-18.32</td>
<td>-18.96</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>T, K</th>
<th>298</th>
<th>338</th>
<th>343</th>
<th>348</th>
<th>353</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_a), kJ·mole(^{-1})</td>
<td>4.13</td>
<td>9.77·10(^{-1})</td>
<td>5.84·10(^{-1})</td>
<td>1.90·10(^{-1})</td>
<td>-2.04·10(^{-1})</td>
</tr>
<tr>
<td>(\Delta \mu_a), kJ·mole(^{-1})</td>
<td>12.97</td>
<td>13.74</td>
<td>13.97</td>
<td>14.18</td>
<td>14.38</td>
</tr>
<tr>
<td>(\Delta S), J·mole(^{-1})·K(^{-1})</td>
<td>5.35</td>
<td>-32.70</td>
<td>-36.06</td>
<td>-39.25</td>
<td>-42.34</td>
</tr>
</tbody>
</table>

Note: * - The heat content and other thermodynamic values are given to the value of kJ·kg\(^{-1}\) of the mixture
According to the data given in Table 1, it can be assumed that the low contribution to the heat content of the mixture is due to the ionic nature of the bonds formed, i.e. the complexes formed between thiosulfate ions, water molecules and selenate ions have high solubility, the bonds have an electrostatic nature. This is reflected in the general physico-chemical characteristics of the mixture (Table 2).

It is shown that the heat content of the mixture decreases with increasing temperature, and the process of heat accumulation is intensified only when the mixture is heated to a temperature of 353 K. The rise in temperature leads to an increase in the number of interactions between water molecules and a decrease in the proportion of tetrahedrally ordered solvent molecules. Heating promotes the process of ion association in systems [18]. It is also known that in equilibrium high-water crystalline hydrates, the first sphere of metal and anion ions is completely filled with water molecules. Therefore, sharp differences in the electrical conductivity of the mixture with infinite dilution and experimental data are associated with the formation of complex ion-aqueous rather than ionic groupings.

According to the ion-plasma interaction model, the activity coefficients should increase with increasing temperature, however, the experimental indices indicate a reverse process of lowering the activity coefficient when the melt is heated up to 12 °C above the melting point, which confirms the hypothesis of an increase in inter-ion interaction, which prevails over the thermal motion of the ions and molecules. Therefore, in order to take into account the interionic interaction in concentrated solutions with the addition of sodium tellurate, the formula stated earlier was modified, i.e. the reference frame from the solvent to the melt (matrix) has been changed [19]. Table 3 gives data on the temperature dependence of the association value and the activity coefficients of the mixture and the addition of sodium tellurate.

<table>
<thead>
<tr>
<th>T, K</th>
<th>( b \times 10^3 )</th>
<th>( \ln \gamma_i )</th>
<th>( \ln \gamma_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>5.753</td>
<td>-0.774</td>
<td>5.753</td>
</tr>
<tr>
<td>338</td>
<td>-2.673</td>
<td>-0.797</td>
<td>-2.673</td>
</tr>
<tr>
<td>343</td>
<td>-2.631</td>
<td>-0.805</td>
<td>-2.631</td>
</tr>
<tr>
<td>348</td>
<td>-2.489</td>
<td>-0.814</td>
<td>-2.489</td>
</tr>
<tr>
<td>353</td>
<td>-2.113</td>
<td>-0.822</td>
<td>-2.113</td>
</tr>
</tbody>
</table>

It is shown that at a ratio of 1:50, the ratio of the practical coefficient of activity of the solution to the theoretical activity coefficient (calculated according to the third Debye-Hückel approximation) decreases with increasing temperature, this indicates the process of heat release. So, according to the Debye-Hückel theory for electrolyte solutions, the increment in the change in the coefficient of activity with temperature is the heat content of the electrolyte solution. It is shown that the more the activity coefficient or degree of association or the chemical potential of the electrolyte changes with increasing temperature, the higher the amount of accumulated heat due to associative formation is. From the kinetic point of view, the process of heat release will be limited by the diffusion of ions (charge carriers) in the volume of the solution from the heated region to the vessel wall, and with the thermodynamic activity of the second component (additive), the activity value being the most informative characteristic of the solution, the chemical potential of the system as a whole, when the external conditions change. Thus, the process of heat accumulation in crystalline hydrate melts is directly proportional to the activity coefficient of the additive component and is of an electrochemical nature. Table 4 shows the results of calculating the contribution of sodium tellurate to the thermodynamic characteristics of the heat accumulation process.

<table>
<thead>
<tr>
<th>T, K</th>
<th>( \ln a_i )</th>
<th>( \Delta G_{\text{m}} ), kJ mol(^{-1})</th>
<th>( \Delta H_{\text{m}} ), kJ mol(^{-1})</th>
<th>( \Delta S_{\text{m}} ), J mol(^{-1}) K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-2.26</td>
<td>5.60</td>
<td>-17.91</td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>-2.28</td>
<td>6.42</td>
<td>-18.81</td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>-2.29</td>
<td>6.54</td>
<td>-19.46</td>
<td></td>
</tr>
<tr>
<td>348</td>
<td>-2.30</td>
<td>6.66</td>
<td>-20.11</td>
<td></td>
</tr>
<tr>
<td>353</td>
<td>-2.31</td>
<td>6.73</td>
<td>-20.59</td>
<td></td>
</tr>
</tbody>
</table>

Note: * - The heat content and other thermodynamic values are given to the value of kJ kg\(^{-1}\) of the mixture.
It can be seen from the data in Table 4 that at high temperatures the contribution to the change in the amount of heat is negative, i.e. sodium tellurate, in the course of reaction with solvent molecules and thiosulfate ions, releases heat into the system, therefore, when sodium tellurate is added to the solution, sodium molecules bind the solvent molecules [20] and thiosulfate ions to stronger complexes, which requires energy, so at low temperatures there is an endothermic process, further, when the influx of heat increases, the associative ability of tellurate increases, as evidenced by negative values of entropy. Those regions with a higher density of matter and, correspondingly, regions whose density approximates the density of the solvent appear in the system. Therefore, the thermodynamic characteristics of the interaction of the components in the mixture were determined (Table 5).

<table>
<thead>
<tr>
<th>T, K</th>
<th>298</th>
<th>338</th>
<th>343</th>
<th>348</th>
<th>353</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ina_t</td>
<td>-2.00</td>
<td>-5.13</td>
<td>-5.17</td>
<td>-5.18</td>
<td>-5.09</td>
</tr>
<tr>
<td>L_2 J.kJ.mole^-1</td>
<td>-40.72</td>
<td>-5.62</td>
<td>-1.24</td>
<td>3.14</td>
<td>7.53</td>
</tr>
<tr>
<td>Δμ_2 J.kJ.mole^-1</td>
<td>4.97</td>
<td>14.41</td>
<td>14.74</td>
<td>14.97</td>
<td>15.17</td>
</tr>
</tbody>
</table>

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

In this case, when sodium tellurate is added in an amount of 1:50 to the base salt, the heat content and heat capacity of the mixture increase. It is shown that during the heating to the melting point (51-55 °C) the system still releases heat into the environment due to the decomposition of the salt associates and the additive with the solvent. However, when the temperature reaches 348 K, the system passes to the heat storage regime, i.e. the heat content changes sign from negative to positive, and with increasing temperature the endothermic effect increases. According to the calculations, this mixture is characterized by a high heat capacity (2400 J/mol·K), therefore, when the temperature reaches 353 K, the system accumulates the maximum amount of heat that is released into the environment with subsequent cooling. Calculations showed that cooled from 353 K to 298 K the mixture emits into the environment 88 kJ/kg, which is more than the value determined by the thermocouple measurements. Probably, there is an error and the loss of heat or changes in the thermal conductivity of glass and air is not taken into account. Also, the contribution of tellurate ion to the heat content of the mixture is calculated, it is shown that the presence of a 50-fold excess of the basic salt contributes to the formation of the most thermodynamically advantageous structure in which tellurate ions are the binding centers of the solvent molecules (so-called associate nodes). On the other hand, when it is heated, the chemical potential increases (assumes positive values). Also, the increase in entropy increases during heating.

Thus, the optimal conditions for achieving the maximum heat-accumulating effect of mixtures containing sodium selenate from the thermodynamic position is the high activity of the components of the additive forming the complexes due to hydration energy, ion-dipole interaction with solvent molecules. The temperature of transition to the active state is 353 K. As a result of the studies, optimal conditions have been found: heating to T = 348 K, stabilizing the effect of tellurate ion on the associates of sodium thiosulfate with water molecules, which together allows to accumulate the energy coming to the system, followed by its release during cooling.

REFERENCES


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НАТРИЙ ТИОСУЛЬФАТЫ НЕГІЗІНДЕК КОМПОЗИТТЕРДІҢ ЖЫЛУДЫ ШОҒЫРЛАНДЫРУ ТЕРМОДИНАМИКАСЫНА НАТРИЙ СЕНАЛАТЫ МЕН ТЕЛУРАТЫНЫҢ ЕСЕРІН БАҒАЛАУ

Аннотация: Колкіті, тұрғын ұйқерді пайдалану процессінде материалдардың толықтының негізгі себебі сыртқы және ішкі температураларының айырмасы, долыр екі температуралық режимдің және қалдықты құрылымның ауырымда, энергияны ұтындайды эртұрлі екілі болады. Сондықтан, екінші нүкте қосылданыс және қосылданыс нысандары мен натрий телуратының есері түшінеді. Температуралардың самптығы сақтау құрылымдарының құрылысын қамтамасыз ететін қаралады.

Наратис көпсіздігі натрий телураты және натрий селена тыныс көпсіздігінің натрий тионосульфатынан конгруэнтті дейін алынғаны және натрий телуратының нысандары болып табылады. Ерекшеленген натрий телураты және натрий селена тыныс көпсіздігінің натрий селенатының және натрий телуратының есері түшінеді. Температуралардың самптығы сақтау құрылымдарының құрылысын қамтамасыз ететін қаралады.

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ОЦЕНКА ВЛИЯНИЯ СЕЛЕНАТА И ТЕЛЛУРАТА НАТРИЯ НА ТЕРМОДИНАМИКУ АККУМУЛИРОВАНИЯ ТЕПЛА КОМПОЗИТАМИ НА ОСНОВЕ ТИОСУЛЬФАТА НАТРИЯ

Аннотация: в процессе эксплуатации транспорта, жилых помещений основной категорий изюса материалов является перепад температур внешних и внутренних, именно высокий градиент и циклические изменения температурного режима приводят к изменениям в структуре материалов, к росту потребления энергии. Поэтому актуальной проблемой наряду с разработкой теплоаккумулирующих материалов позволяющих существенно снизить теплопотери в окружающую среду, является модификация матрицы посредством введения различных добавок. Цель работы заключается в установлении влияния добавки теллурата натрия и селената натрия на пентагидрат тиосульфата натрия на теплоаккумулирующие свойства полученных смесей. Исчение поведения селената натрия и теллурата натрия в составе смеси с кристаллогидратом тиосульфата натрия проводилось кондуктометрическим методом. Рассчитаны изменения коэффициентов активности селената натрия, вклада селената натрия в теплосодержание смеси с пентагидратом тиосульфата натрия. Также рассчитаны изменения коэффициентов активности и степени ассоциации смеси теллурата натрия – пентагидрат тиосульфата натрия (1:50), согласно которым процесс образования сложных комплексов является экзотермическим, процесс аккумулирования тепла имеет электростатическую природу. Следовательно, прочность ассоциатов снижается при повышении температуры. Также выявлено что смесь охлаждается до T=298 К выделяет в окружающую среду до 100 кДж/кг, Температурой перехода в активное состояние является 353 К. В результате проведенных исследований найдены оптимальные условия: нагрев до T=348 К, стабилизирующий эффект теллурат-иона на ассоциации тиосульфата натрия с молекулами воды, что в совокупности позволяет накапливать энергию поступающую к системе, с последующим ее выделением в ходе охлаждения.

Ключевые слова: пентагидрат тиосульфата натрия, селенат натрия, теллурат натрия, коэффициенты активности, теплосодержание, расплав кристаллогидрата, электропроводность

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