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Sh.K.Amerkhanova[1], V.D.Alexandrov[2]

[1]*Ye.A.Buketov Karaganda State University;*
[2]*Donbas National Academy of Civil Engineering and Architecture, Ukraine*
(E-mail: amerkhanova_sh@mail.ru)

Evaluation of heat-accumulating properties of organic acids and their composites with REE

In this paper the melting heat of palmitic and stearic acids was defined by the electrochemical method. It was shown that the melting process is accompanied by heat emission. During all time of thermal cycling the behavior of curve is preserved. It is found that for a mixture of palmitic acid and REE melting process is accompanied by changes in the structure of the complex and ion pairs. It was revealed that the heat of fusion of the composite of palmitic acid and cesium chloride is higher than of the organic acid through the formation of crystallization centers with a high melting point. Consequently, the mixture of organic acids containing cesium ions may be recommended as a heat accumulating material.

Key words: heat storage properties, organic acids, palmitic acid, stearin acid, REE, cesium chloride, melting heat, crystallization.

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The heat-storage materials (HAM) based on phase transformations [1–10] are widely used currently in various fields of science and technology, in everyday life. They are used in the instrumentation for removing of heat at high heat loads to protect electronic devices from overheating, to stabilize the room temperature. In the heat power engineering they serve for the rational use of thermal energy and for accumulation of solar heat to smooth daily and seasonal peaks in energy consumption, lowering energy costs, in the heat accumulators for storing and transporting medicines and foods, for supporting the temperature in the cab of cars and railway locomotives etc.

Due to the lack of systematic studies of the influence of different factors on the liquid phase and the kinetics of solidification, the literature data contain a lot of contradiction that hinder the further development of the theory of crystallization of supercooled state and obtaining reliable experimental means of influence on the structure and properties of HAM. For the use as a storage tank there are following requirements to HAM: a phase transition should have a pronounced effect of the latent heat (ability to accumulate large amounts of heat in melting), slight supercooling during crystallization; possess good reproducibility phases transmission properties over a large number of thermal cycles, the phase transition should occur near real melting temperature, and they must be affordable and accessible; there should comply with health and environmental safety; there packing in a container and the container material must provide the best conditions for the transfer of heat.

The aim of the work is to determine the specific heat of fusion of organic acids and composites with REE. Therefore highly relevant is the assessment of latent heat of fusion of organic substances and modification of REE.

Experimental part

The determination of the specific heat of fusion was carried out by method [11]. The samples were heated by convection. Temperature control was carried out with a thermometer, which was immersed in the sample with visual and thermal analysis thermocouple (chromel-alumel) at measuring the thermal-EMF. Response function is the value of thermo-EMF.

Materials and Reagents. Palmitic and stearic acid used as the main objects, cesium chloride used as REE. Reagents were used of next classification (pure for analysis, reagent grade). Thermo-EMF was recorded using a voltmeter brand EV2265-1. Ratio of amount organic acid to amount REE is 1000:1.

Discussion of results

The results of thermo-EMF measurements for samples of organic acids and their mixtures with REE are depicted in Figures 1–3.

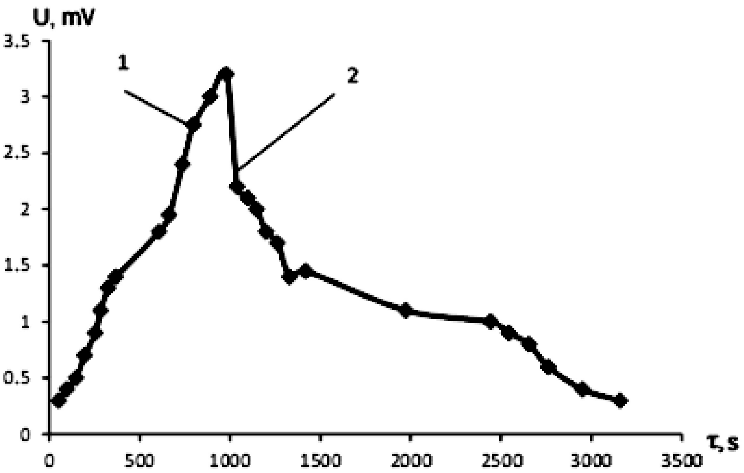

Figure 1. Change of thermo-EMF of chromel-alumel thermocouple in the melting process of palmitic acid

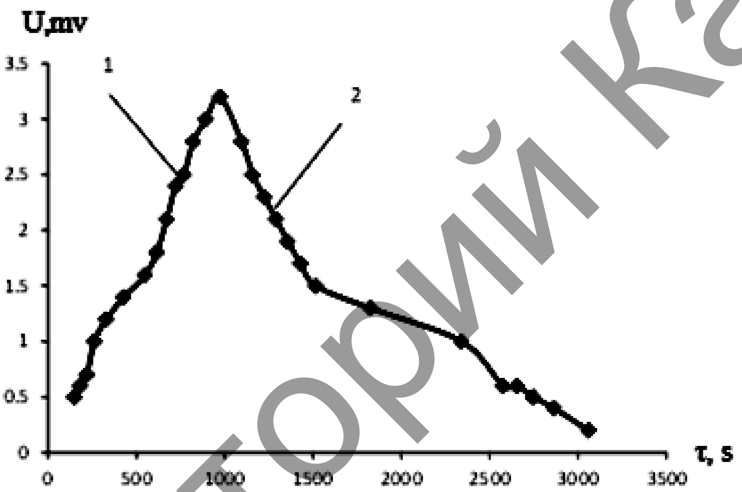

Figure 2. Change the thermo-EMF of chromel-alumel thermocouple in the melting process of palmitic acid with the addition of CsCl (the ratio of HL:CsCl is 1000:1)

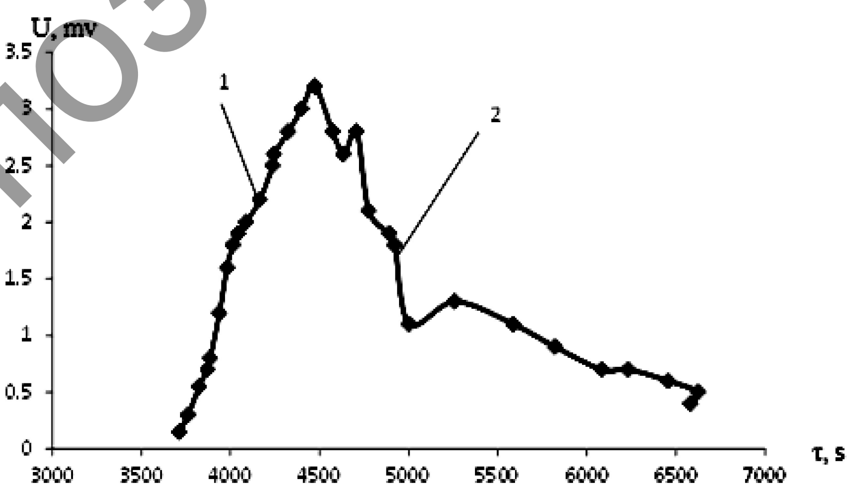

Figure 3. Change the thermo-EMF of chromel-alumel thermocouple in the melting process of stearic acid (second thermal cycle)

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Kinetic curves of the heating and cooling of palmitic acid and mixtures with REE allow to judge the existence of several sections of the equilibrium and non-equilibrium explosive crystallization in which there is increased potential difference. So for the palmitic acid this process proceeds in interval 0.5–3.5 mV, which corresponds to 25–95 ºC. As known, the difference in potential between metals with different thermal conductivity is due to the speed of electrons under the action of heat and the presence of traps in the metal connected with defects in the crystal lattice. The difference in the electrochemical potential of electrochemical circuit is due to various reaction ability of solution compounds or chemical reaction. Consequently, the cause of the current in the circuit might be the temperature and chemical potential.

In work [12] the process of melting mixtures of palmitic and stearic acids in a wide range of compositions was studied. It is shown that a mixture comprising 0.75 mole palmitic acid and 0.25 mole stearic acid is eutectic melt at 325 K, the melting enthalpy is 49.58 kJ/mole. This value is the maximum from two eutectics; this fact suggests the presence of a sufficiently high heat storage capacity, because of formation of chemical bonds between mixture components. I.e. melting heat is directly related to the strength of chemical bonds between the associates in the case of single-component system, between different substances in the case of a multicomponent system. Therefore, data of the thermo-EMF was calculated value of the specific heat of melting (crystallization) of palmitic and stearic acids (Table). It's shown that crystallization process is exothermic, and results according to literature data [13].

Table

Results of calculation of specific melting heat of palmitic, stearic acids and palmitic acid with CsCl

Acid	Segment of the curve $T=f(\tau)$	τ, s	T, C	λ, J/kg·K	Process	The rate of heat output, J/(kg·s)
Palmitic acid	A	1045	80.00	214132	Cooling the melt	5.66
	B	1380	57.73		Crystallization of substance	
	C	1715				
	D	2050	52.37		Cooling of solid state	
Stearic acid	A	4736	83.59	252932	Cooling the melt	6.11
	B	5126	54.73		Crystallization of substance	
	C	5516				
	D	5906	47.82		Cooling of solid state	
Palmitic acid with CsCl	A	942	80.27	295233	Cooling the melt	3.93
	B	1532	58.95		Crystallization of substance	
	C	2123				
	D	2713	44.35		Cooling of solid state	

As seen from Table, the value of the specific melting heat of mixture is above that of pure substance (solvent). Therefore, for enhancing the strength of chemical bonds between the components of fusion must be substances having donor-acceptor properties, as such alkali metal salts with a high value of crystal radius, namely, rubidium and cesium, which are the most powerful electron acceptors and can form a stable ion pair in the absence of polar solvent [14].

In this case, the melting process of mixture is accompanied by the formation of separate nucleation having higher internal energy and having a higher melting point. From the literature it is known that alkali metals have a higher melting temperature, which is decreased during transition from cation with low radius to cation with high radius in the case of inorganic salts. Therefore, supplementation with a higher melting point of either direct synthesis in the melt blend is method of increasing of heat-accumulating ability of materials [15].

Conclusion

Thus, as a result of studies, the melting point of palmitic and stearic acids and their mixtures with cesium chloride were determined. The specific melting heat of mixture (palmitic acid:REE) was calculated, it is shown that melting process of mixture proceeds in several stages, and the system has the type «fusion-solution». The melting heat of mixture with cesium chloride is higher than with palmitic acid, hence the addition of cesium chloride enhances heat storage properties of the organic substance.

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Ш.К.Әмерханова, В.Д.Александров

Органикалық қышқылдар және олардың СЖЭ мен композиттерінің жылушоғырландырғыш қасиеттерінің бағалануы

Мақалада пальмитинді және стеаринді қышқылдарының балқу жылулары электрохимиялық әдіспен анықталды. Балқу процесі жылу бөлінумен жүретіні айқындалған. Термоциклдандырудың барлық уақыты бойынша қисық жолы сақталған болатын. Пальмитин қышқылы мен СЖЭ қоспасы үшін балқу процесі комплекс құрылысының және ионды буларының өзгеруімен жүретіні байқалған. Жоғары балқу температурасы бар кристалдану орталықтарының қалыптасу арқасында органикалық қышқылға қарағанда цезий хлориді қосылған пальмитин қышқылы композитінің балқу жылуы жоғары екені белгіленген. Демек, құрамында цезий иондары бар органикалық қышқылының қоспасын жылушоғырландырушы материал ретінде ұсынуға болады.

Ш.К.Амерханова, В.Д.Александров

Оценка теплоаккумулирующих свойств органических кислот и их композитов с РЗЭ

В статье электрохимическим методом определены теплоты плавления пальмитиновой и стеариновой кислот. Показано, что процесс плавления сопровождается выделением теплоты. В течение всего времени термоциклирования ход кривой сохраняется. Установлено, что для смеси пальмитиновой кислоты и РЗЭ процесс плавления сопровождается изменением структуры комплекса и ионных пар. Выявлено, что теплота плавления композита пальмитиновой кислоты с хлоридом цезия выше, чем для органической кислоты, за счет формирования центров кристаллизации с высокой температурой плавления. Следовательно, смесь органической кислоты, содержащая ионы цезия, может быть рекомендована в качестве теплоаккумулирующего материала.

Репозиторий КарГУ