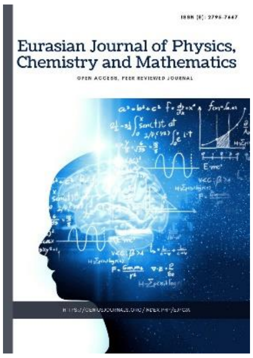

A Derivatographic Method for Determining the Kinetic Parameters of Thermal Degradation of Developed Ion-Exchange Materials

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ABSTRACT

The article describes the application of the derivatography method for the developed ion-exchange materials in order to determine the kinetic parameters of the thermal degradation process. The methods of calculation of the main kinetic parameters – the activation energy and the order of the thermal degradation reaction of ion-exchange materials according to thermogravimetric analysis are presented. It is revealed that the destructive processes of ion-exchange materials belong to the reactions of the first order. It is determined that the developed ion-exchange materials are at the same level in terms of thermal stability and the nature of their decomposition can be explained by the destruction of the corresponding bonds.

Keywords: thermal stability, thermogravimetric analysis, rate of destructive process, ion exchange materials, activation energy, reaction order.

Introduction

Ion-exchange materials are widely used in thermal power engineering, hydrometallurgy, chemical and food industries. Technological processes using ionites, including the stages of their regeneration, are carried out in some cases at elevated temperatures, therefore, the nature and intensity of thermal destruction of ionites are of great practical importance.

In the study of the thermal stability of ionites, the mass spectrometric method is mainly used, as well as a method based on heating a sample in an inert gas current and determining the temperature of destruction of ionite functional groups. The thermal stability of ionites determines their resistance to the processes of destruction (destruction of the ionite matrix) and degradation (cleavage of functional groups from the ionite framework). The main indicators of ionite quality are physical properties, chemical and thermal stability, working exchange capacity, etc.

The research comprehensively examines the issues of thermal stability of the developed ionites using the method of dynamic thermogravimetry [1], which consists in registering the mass of the sample depending on temperature when it is heated at a certain speed. The process proceeds in two directions of chemical transformations and thermal destruction. A variable in thermogravimetric analysis is the mass of the material being destroyed by the sample.

Research methods

Investigation of the thermal stability of ionites conventionally designated AR&ISM-8 and AR&ISM-9 based on products by the interaction of PEPA using a chemically modified product (product-A) AR&ISM-9 and without it AR&ISM-8 and aldehyde [2-4] using dibasic dicarboxylic aromatic acid (DDAC) and The study of their catalytic activity was carried out on a DTG-60 device manufactured by Shimadzu (Japan). The 5 mg sample was heated from 20 to 800℃ at a heating rate of 10℃/min. The analysis was carried out in an atmosphere of inert gas – argon, at a feed rate of 80 ml/min. Powdered aluminum oxide II (Al_2O_3) was chosen as the reference for comparison.

A variable in thermogravimetric analysis is the mass of ionite being degraded. The kinetic parameters of the TG curve are based on a formal kinetic equation:

$$-\frac{dM}{dT} = kM^n$$

where M - the mass of the sample that reacted; k - the reaction rate constant; n -the reaction order; T - the temperature. This equation describes the kinetics of thermal decomposition of solids very well. The dependence of the reaction rate constant on temperature is described by the Arrhenius equation:

$$-\frac{dM}{dT} = A \cdot \exp\left(-\frac{E}{RT}\right) M^n$$

where A - the pre–exponential multiplier; R - the universal gas constant; T - the temperature.

The process of thermal decomposition of AR&ISM-8 and AR&ISM-9 is a complex process that consists of a series of sequential and parallel reactions, and the Arrhenius equation cannot be applied to determine the kinetic parameters with sufficient accuracy. Among the methods for determining the kinetic parameters of thermal degradation of compounds based on mathematical processing of TG curves, the Freeman and Carol method has found the greatest application [5].

According to this method, for the current decomposition rate $\omega\tau$ of condensed matter corresponding to temperature T, the expression is valid at a given time τ:

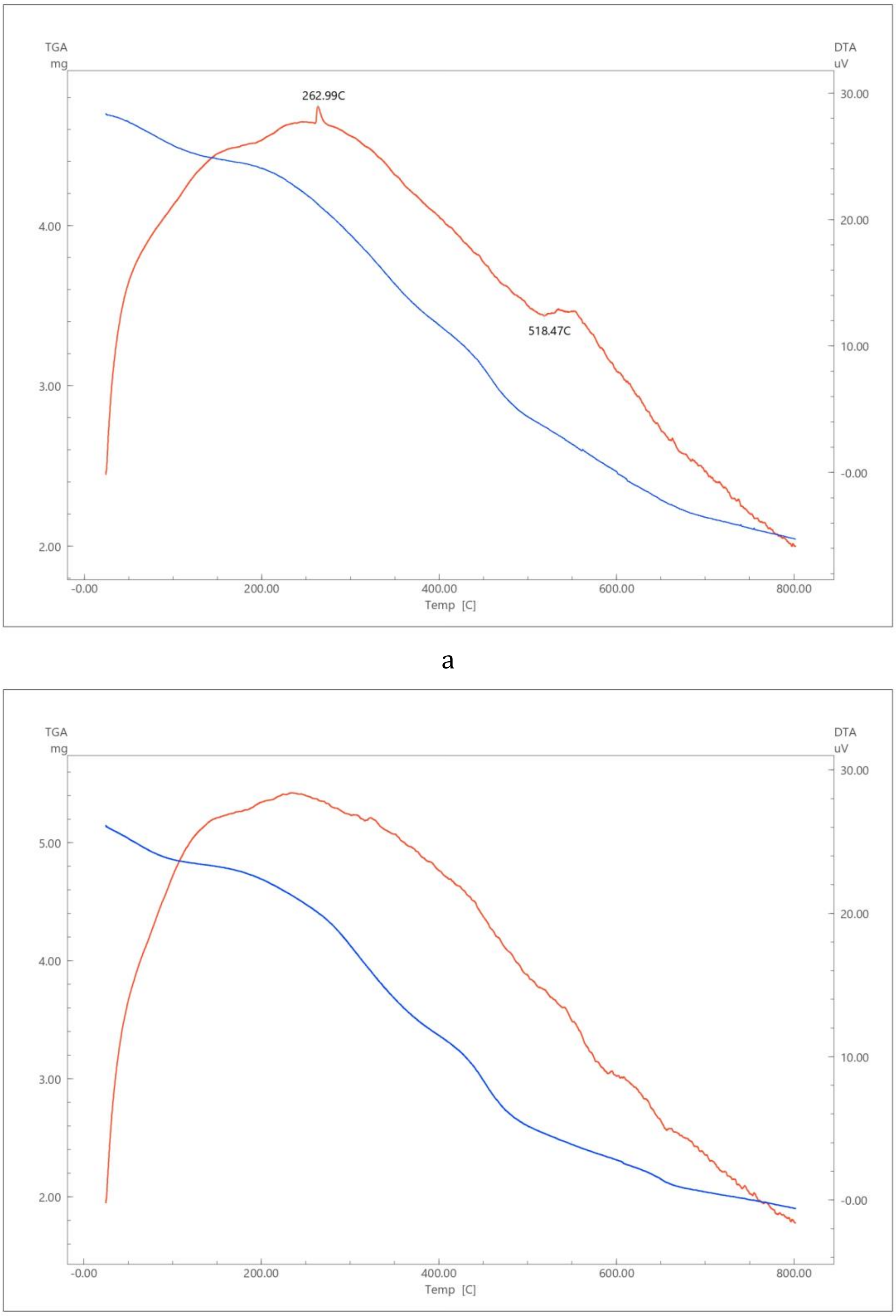
$$\omega_T = \frac{dM}{dT} = \frac{Z}{\beta} \cdot e^{\frac{E_a}{RT}} \cdot M^n$$

where M - the mass of the sample that reacted; T - the temperature, Z - the preexponent in the Arrhenius equation, β - the heating rate, R - the universal gas constant.

Using the linearization of the initial data by the Freeman-Carroll method, the values of the activation energy E_a and the reaction order - n were found.

Results and discussion

The thermal properties (thermogravimetric analysis – TGA and differential thermal analysis of DTA) of synthesized ionites AR&ISM-8 (DDAK : PEPA : furfural) and AR&ISM-9 (DDAK : PEPA : Product-A : furfural) were investigated. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of synthesized samples are shown in figure 1.



a

b

Figure 1. TGA and DTA of ion exchange materials AR&ISM-8 (a) and AR&SM-9 (b)

Thermogravimetric studies have shown that the heating process of ion exchange materials AR&ISM-8 and AR&SM-9 is accompanied by various endothermic and exothermic effects. As can be seen from the graphs of the DTA, the first endothermic effect can be attributed to the dehydration of ion-exchange materials. The cleavage of the functional groups of the studied ionites begins at temperatures of the order from 260 ° C to 520

° C, which corresponds to the second endothermic peak. The frame of the ion-exchange material AR&ISM-9 is more resistant to temperatures.

Considering that the initial ionite samples taken for TGA had different values, it was advisable to construct a dependence of mass loss as a percentage of temperature based on the mathematical values of TGA (figure 2). Thus, thermogravimetric curves of ionites showed a slight weight loss of up to 2% at 64 and 48 ° C, explained by the loss of ionite moisture. According to the curves, it can be observed that the decomposition of ionites begins with a 5% weight loss at a temperature of 115 °C for AR&ISM-8 ionite and 88°C for AR&ISM–9 ionite (table 1.). The decomposition temperature of ionites at 50% mass loss is 630 and 507 °C, respectively.

Table 1.
Results of thermogravimetric analysis of ionite mass loss from temperature

Ion exchange material	Mass loss (%) of temperature (°C)						
	2%	5%	10%	20%	30%	40%	50%
AR&ISM-8	64	115	241	330	419	496	630
AR&ISM-9	48	88	216	301	360	440	507

Comparing the thermogravimetric curves of the two ion-exchange materials (figure 2), it can be seen that the temperature of the onset of thermal degradation in AR&ISM-8 is lower than in AR&ISM-9. As is known, an alternative and additional representation is the use of the first derivative of the TGA curve in temperature or time. To interpret the TGA data, derivative functions of the TG curves were obtained and the dependences of the rate of change in the mass of samples on time and temperature were derived (figure 3).

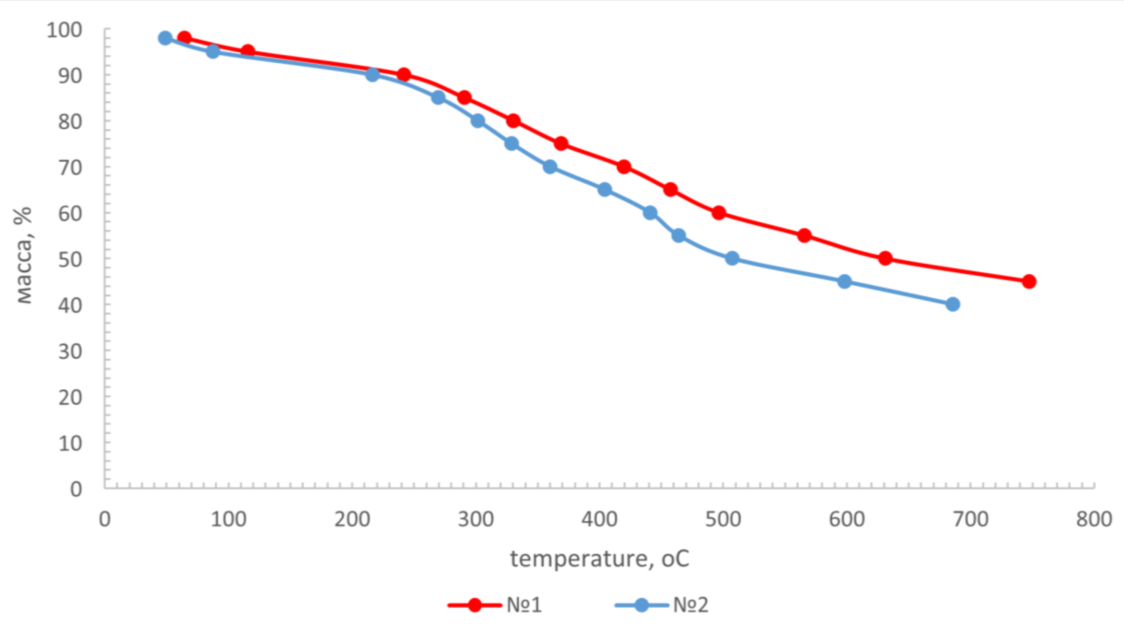
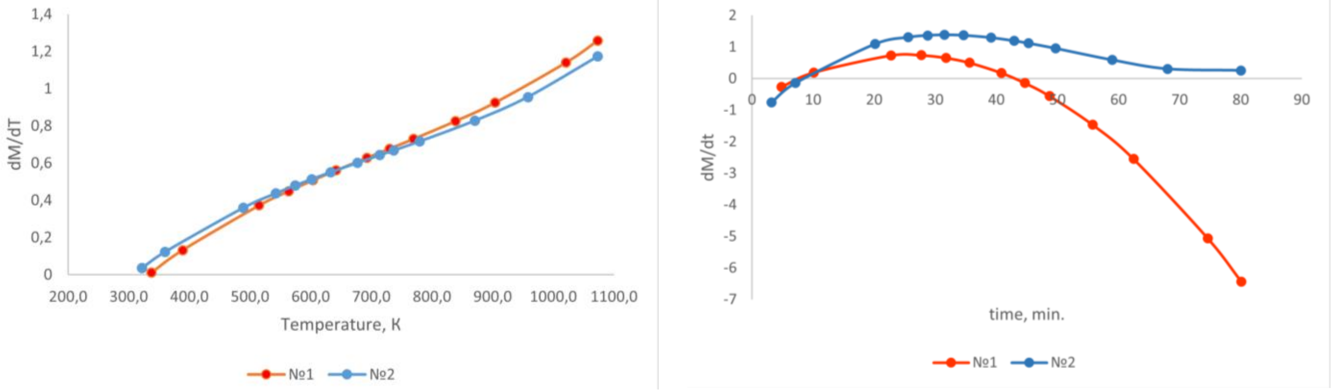


Figure 2. Graph of the dependence of the mass loss of ion-exchange materials AR&ISM-8 (1)_ and AR&SM-9 (2) of temperature

Studies have shown (figure 3) that there are no obvious differences in the indicators of mass loss from temperature but still it can be noted that in the sample AR&ISM-8, the rate of mass change from temperature at the initial stage of destruction is less intense than in AR&ISM-9. At a temperature of 320-420°C, the rate of the destructive process is almost the same for the two ionites, and further, at temperatures above 420°C, a difference in the process is observed. The difference in the rate of the destructive process can be observed by the curves of the rate of change in the mass of samples from time at temperatures above 100ºC. The rate of the destructive process in AR&SM-9 is more intense than in AR&ISM-8 and is explained by the chemical structure of the ion-exchange materials under consideration. At the same time, the polymer frame of the AR&ISM-8 "stitching" is more durable. A study of the dependence of the rate of mass loss on time showed that in AR&ISM-9, the onset of the rate of mass loss is detected already at 20-25 minutes, and in AR&ISM-8 this indicator manifests itself at a time interval of 30-35 minutes, and the curve is much "lower" than in AR&ISM-9, which indicates a lower speeds and at high temperature ranges. This could be limited to concluding about the thermal stability of the ion-exchange materials under consideration.



a b

Figure 3. The rate of destructive process of ion exchange materials AR&ISM-8 (1) and AR&ISM-9 (2) a) on temperature, b) on time

However, for a more in-depth study of the thermal stability of ion-exchange materials and TGA, it is necessary to calculate the kinetic parameters, in particular, the calculation of the activation energy and the reaction order of the thermodestructive process. To do this, we derive the function of the curve of dependence of the mass of the sample that reacted on temperature (figure 4), and calculate the derivative of this function. The derivative of the mass loss curve function with respect to temperature determines the rate of decomposition of condensed matter with respect to temperature – $\omega_T = \frac{dM}{dT}$.

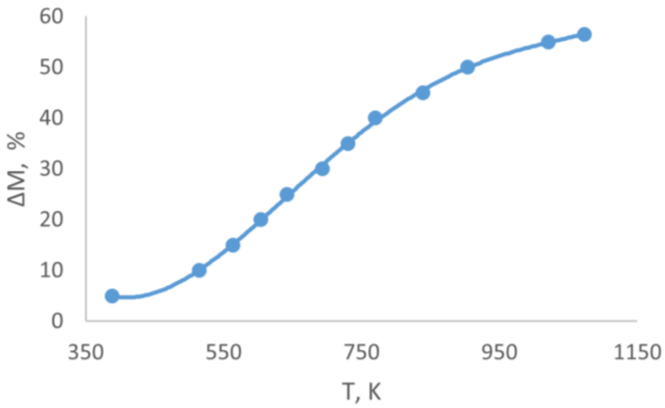
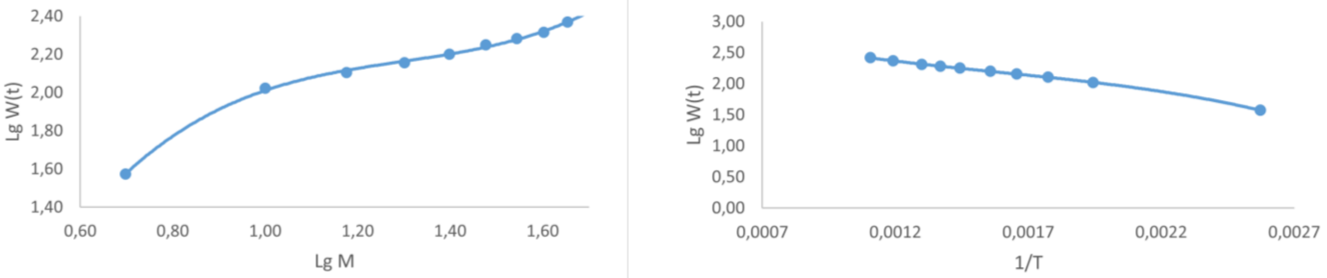


Figure 4. Dependence of mass loss on temperature for sample A R&ISM-8

Since the heating rate β is unchanged, the decomposition rate of the condensed matter in time is equal to – $\omega_\tau = \omega_T \cdot \beta$. Based on the data obtained, we build a logarithmic dependence $\lg\omega_T = f\lg M$ (figure 5 a) and semi – logarithmic $\lg\omega_\tau = f({}^{1}/_{T})$ dependence (figure 5b).



a) $lg\omega_T = f lgM$

b) $lg\omega_\tau = f(^1/_T)$

Figure 5. Logarithmic (a) and semi-logarithmic (b) dependence of the decomposition

Thus, from one TG curve for each point of mass loss, depending on $\lg\omega_T$ from $\lg M$, we find the tangent of the angle of inclination at the corresponding points, this will correspond to the value of the reaction order – "n". And according to the dependence $\lg\omega_\tau$ from $^1/_T$ – we find the value of the activation energy by the formula $E_\alpha = 2{,}303 \cdot R \cdot tg\alpha$, for the corresponding point of mass loss.

It is known that if the reaction is complex, then a number of intermediate transformations occur and the reaction order is equal to the reaction order of the limiting stage. In studies, the limiting stage of the reaction – decomposition of ion-exchange materials refers to reactions of the first order.

After analyzing the results of the analysis and the calculated data, it can be noted that the behavior of the developed ion exchange materials is almost the same. The nature of their decomposition can be explained by the destruction of azomethine, simple oxygen and ester carboxyl bonds. Research (Table2) show that with increasing temperature, the activation energy decreases, and the reaction of destructive processes of ion-exchange materials at high temperatures is about 50% and this does not affect the technological processes of using the developed ion-exchange materials.

Table 2.
Kinetic parameters of the destruction process of ion-exchange materials AR&ISM-8 and AR&SM-9

Weight loss in %	Kinetic parameters			
	AR&ISM-8		AR&ISM-9	
	n-the reaction order	E_a, kJ kJ/(molK)	n-the reaction order	E_a, kJ kJ/(molK)
10	0,46	2,49	0,48	2,22
15	0,42	5,96	0,32	3,76
20	0,45	7,08	0,31	5,56
25	0,63	9,62	0,38	7,37
30	0,49	5,46	0,57	8,88
35	0,55	8,32	0,50	5,40
40	1,05	14,69	0,33	4,24
45	1,08	8,83	0,67	13,35
50	2,18	20,12	1,51	15,98
55	3,69	6,51	1,65	8,94

Studies have shown that AR&ISM-8 is more thermally stable than AR&SM-9, since the dynamics of the thermodestructive process and the kinetics of thermal decomposition over time are greater than those of the AR&ISM-9 sample. And the lower the activation energy, the faster the reaction goes, in our case, a destructive reaction. It follows from this that the ion exchange material AR&ISM-8 is more heat resistant than AR&SM-9.

Conclusion

1. The kinetic parameters of thermal degradation of the developed ion-exchange materials were determined by the derivatographic method.
2. The kinetic parameters of the developed ion–exchange materials are calculated - the reaction order and activation energy.
3. It was revealed that the studied ion-exchange materials are not inferior in thermal stability to ionites used in technological processes.

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