TEMPERATURE DEPENDENCES OF DYNAMIC PARAMETERS OF WATER IN FOSSIL-COAL PORES

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The results of nuclear magnetic resonance (NMR) studies of water relaxation times, T_1 and T_2, and self-diffusion coefficients, D, in water-saturated pores of fossil coal (anthracite A) are reported. The spin-echo and broad-line NMR measurement techniques were used. The resonance frequency of ^{1}H spins was found to equal $f \approx 20$ MHz in the temperature, T, range from 90 K to room temperature. The results of experiments evidence the existence of a smeared phase transition in the temperature range $T = 180 \div 230$ K. Using the Uo–Fedin technique, the corresponding phase transition energy was estimated to be $U_0 = 27 \div 35$ kJ/mol. The activation energy E_a associated with the $T_2(T)$ dependence was found to increase from 4 kJ/mol at $T = 90$ K to 18 kJ/mol at $T = 300$ K. The deviation of the temperature dependence of the self-diffusion coefficient D from the Arrhenius law was explained by the change-over from the bulk diffusion mode to the surface one as the temperature decreased.

1. Introduction

The variety of physical properties of fossil coal and its chemical composition, which is caused by a quantitative variation in accompanying molecular compounds, characterizes the state of coal beds. The analysis of coal using physical methods is extremely important for forecasting the gas and coal releases, which are probable in the course of coal mining. One of those methods is the nuclear magnetic resonance (NMR) one [1]. It composes an effective way to analyze the structure and the sorption properties of porous sorbents, for instance, fossil coal [1, 2]. Modern NMR spectrometers allow one to measure the relaxation times of proton spins in sorbates containing hydrogen and obtain important information concerning the distributions of pores over their dimensions and the mobility of sorbate molecules in the pore volume [3].

Earlier, using the pulsed and continuous-wave NMR techniques, we studied the processes of sorbate (methane and water) desorption from coal at room temperature [4]. The main purpose of this work was to study the temperature dependences of some parameters (the spin-spin, T_2, and spin-lattice, T_1, relaxation times and the self-diffusion coefficient D), which characterize the mobility of water molecules in anthracite pores. The activation energy values derived from the Arrhenius dependences for those quantities give an idea of the mechanisms of spin relaxation for hydrogen ^{1}H nuclei and the mobility of molecules under a confined geometry of pores.

2. Materials and Methods of Experimental Researches

In this work, we analyze coal of rank A (anthracite bed h^8, "Natalia"; mine "2-2 bis"; the "Shahtarskantratsit" mine office; the yield of volatile substances $V^{\mathrm{daf}} = 4.8\%$; the sulfur content $S \approx 1\%$; and the ash content $A^d \approx 12\%$).

Coal fractions with (2–2.5)-mm particles were saturated with water vapor in an exsiccator at room temperature. Then, the specimens of fossil coal prepared in such a way were used to determine the relaxation times T_1 and T_2, as well as the self-diffusion coefficient D. The measurements were carried out on a wide-line spin-echo spectrometer at the resonance frequency of hydrogen, ^{1}H, nuclear spins, $f \approx 20$ MHz.

As model sorbents, we also studied silica gels with known pore dimensions. Some parameters of model porous sorbents used in our researches are shown in Table 1.

We used sequences of Khan pulses to register the spin-spin relaxation and applied the two-pulse technique of progressive saturation to measure T_1 [5]. For the sake

T a b l e 1. **Characteristics of used model porous sorbents**

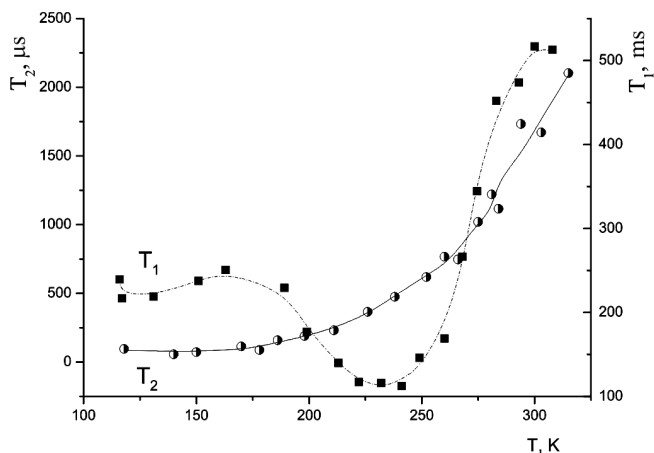| Silica gel	Pore diameter d, nm	Granule shape and size
SK-5a	0.5	cylindrical. $h = 7$–10 mm. $d = 3$ mm
KSK-2	6.5	spherical. $d = 3$ mm
MPS-250	26	spherical. $d = 0.1$ mm
MSA-750	38	spherical. $d = 0.5$ mm

Fig. 1. Temperature dependences of spin-lattice, T_1, and spin-spin, T_2, relaxation times of ^{1}H nucleus spins of water molecules in anthracite pores

of comparison between the results obtained for water-saturated coal using the pulse and autodyne methods, the measurements were also carried out on a stationary NMR spectrometer. The time of spin-spin relaxation, T_2, can be calculated from the width of a line, ΔB, in the Gaussian representation, i.e. $T_2 = 1.41/(\gamma \Delta B)$, where γ is the gyromagnetic ratio for a proton.

Low-temperature measurements were carried out with the use of a flow cryostat, which allowed the temperature in the volume of NMR spectrometer contour to be maintained constant in the range from 90 K to room temperature. At the first stage of the experiment, the minimum temperature was reached. Afterward, the temperature was increased gradually and maintained constant to an accuracy of ± 1 K by means of a temperature regulator. This technique allowed water to be reliably resolved into bulk and bound ones, the procedure being described in works [1, 6] in more details. In such a way, the whole temperature range of the phase transition of water in a porous structure of anthracite into the solid (crystal-like) state was scanned.

When determining T_1 and T_2, the time dependence of the spin-echo signal amplitude was approximated, by making assumption that two proton components associated with the sorbent and water are present. In this case, the spin-echo signal responsible for the spin relaxation of ^{1}H nuclei in the coal substance component containing hydrogen was excluded. In addition, provided that two water states are present, the spin-echo signal responsible for the spin relaxation of ^{1}H nuclei can be resolved into two separate components: for water more coupled (s) with pore walls and less coupled (or free) one (f) in the bulk of large pores.

The self-diffusion coefficient D was calculated by approximating the damping of the spin-echo signal amplitude with the expression

$$I(\tau) = a \exp(-2\tau/T_{2c}) + b \exp(-2\tau/T_{2x}) \times$$

$$\times \exp\{-D(G_0\gamma)^2(2\tau)^3/3\}, \tag{1}$$

where 2τ is the spin-echo delay time with respect to the first pulse, and $G_0 = 0.14$ T/m is the magnetic field induction gradient.

The temperature dependences of the relaxation times T_1 and T_2 and the self-diffusion coefficient D were examined both in the semilogarithmic (Arrhenius) coordinates and in the linear-equation approximation for the temperature dependences of T_1 and T_2, which allowed the activation energy E_a to be determined and a conclusion on the relaxation mechanism at the spin excitation by pulses in the radio-frequency range to be drawn.

3. Results and Their Discussion

Typical dependences for the total times of spin-lattice, T_1, and spin-spin, T_2, relaxation of protons in water (free and bound) in anthracite pores are shown in Fig. 1. As the temperature decreased to $T \approx 225$ K, a reduction of the spin-lattice relaxation time T_1 was observed firstly; then T_1 increased and saturated at a certain constant value. At the point of the T_1 minimum at $T \approx 225$ K, provided the intramolecular dipole-dipole mechanism of spin relaxation, the relation $2\pi f\tau \approx 1$ is obeyed [5], which allowed the correlation time to be evaluated as $\tau \approx 8 \times 10^{-9}$ s.

Near room temperature, the correlation time τ decreased considerably, so that the condition $2\pi f\tau \ll 1$ was satisfied. The mode of rapid relaxation was realized in this case, for which $1/T_1 \sim \tau$ [7]. Analogous temperature dependences of T_1 with a minimum in the given temperature interval were observed for other porous sorbents as well [8]. For anthracite, such a dependence was obtained for both the free (f) and bound (s) components, which testified to a common mechanism of ^{1}H spin relaxation.

The activation energy E_a was calculated from the temperature dependence of the spin-spin relaxation time. The value of T_2 changes from about 13 kJ/mol at high temperatures to about 4 kJ/mol at low ones ($T < 170$ K) (Fig. 2). The reduction of the activation energy E_a, when the temperature T decreases, can be explained by a reduction in the bulk mobility of sorbate molecules and the domination of molecular transport along the

pore surface. In addition, this reduction of the activation energy can be associated with a change of the spin relaxation mechanism in the sorbate, namely, the spin-rotation mechanism of ^{1}H spin relaxation in water molecules becomes active instead of the translational dipole-dipole one [9].

The diffusion coefficient of water, D, in anthracite pores increases, when the temperature T decreases (Fig. 2), which takes place owing to the change of the mobility mechanism for water molecules and the presence of water in several phase states in the pore volume. The averaged diffusion activation energy E_a was evaluated for moisture-saturated anthracite specimens from the temperature dependence of D, plotted in the Arrhenius coordinates, at high temperatures ($T > 170$ K) to obtain 27 kJ/mol. Notice that a value of 52 kJ/mol was obtained for the same coal with a natural moisture content, which evidences the presence of the strongly bound water component. An observable deviation of the temperature dependence for the self-diffusion coefficient D from the Arrhenius one at $T \approx 170$ K can be explained by the change-over from the bulk to surface diffusion mechanism, as the temperature decreases [10].

Note that a good correspondence was observed between the data obtained using the spin-echo and continuous-wave NMR techniques. For instance, at $T = 294$ K, the time of spin-echo relaxation T_2 for bulk water was estimated from the NMR line width, $\Delta B \approx 0.185$ G, to be $T_2 = 1.41/(\gamma \Delta B) \approx 1790$ μs, whereas the spin-echo method gave the value $T_2 \approx 1732$ μs.

The results obtained using two NMR techniques testify to the presence of a "smeared" phase transition of water in coal (anthracite) pores in the temperature interval of 180–230 K. The energy of this phase transition was evaluated in the temperature interval $T \approx 180 \div 230$ K with the use of the Uo–Fedin formula [11]

$$U_0 \ [\text{kJ/mol}] = 154.5T$$

T a b l e 2. Experimental values of longitudinal relaxation time T_1 and diffusion coefficient D at various temperatures T for sorbed (s) and free (f) water fractions in anthracite pores

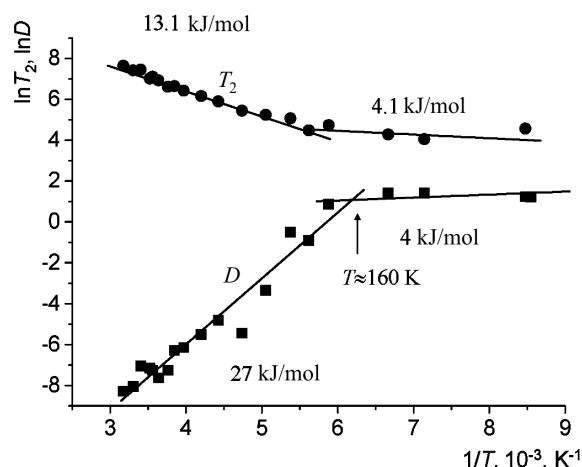| T, K	T_{1s}, ms	D_s, 10^{-10} m^2/s	T_{1f}, ms	D_f, 10^{-9} m^2/s
283	77.2	1.93	892	2.23
274	61.7	1.54	692	1.73
266	66.3	1.66	871	2.18
260	60.7	1.50	412	1.04
252	60.9	1.50	572	1.43
238	–	–	199	0.50
227	–	–	269	0.67

Fig. 2. Temperature dependences of the spin-spin relaxation time of ^{1}H nucleus spins, T_2, and the self-diffusion coefficient of water, D, in the bulk of anthracite pores

to obtain $U_0 \approx 27 \div 35$ kJ/mol.

In the temperature range above the minimum point $T \approx 220$ K (Fig. 1), the coefficients of translational diffusion D can also be estimated from the measured T_1-values. Provided the intramolecular dipole–dipole mechanism of relaxation, the relation between the coefficient of translational diffusion D and T_1 is $D = 0.25 \times 10^{-8} T_1$ m/s^2 [4], where T_1 is expressed in seconds. As a result, the NMR relaxation could be resolved into two contributions, which corresponded to sorbed and free (bulk) water in the pores. Table 2 exposes the measured T_1-values and the calculated diffusion coefficients D for sorbed (s) and free (f) water in anthracite pores at various temperatures within the interval $T = 211 \div 283$ K.

For free water, the corresponding D-values are higher by approximately one order of magnitude than those for sorbed one. The activation energies E_a estimated on the basis of the data obtained are 4.1 ± 1.9 kJ/mol for sorbed (s) water and 13.1 ± 2.2 kJ/mol for free (f) one. A higher activation energy for free water testifies to a higher mobility of molecules far from the pore surface, whereas the lower activation energy corresponds to the fact that the sorbed water molecules possess only the rotational degree of freedom near the active center.

For anthracite, which is characterized by the smallest pore diameter in the coal metamorphism series, the U_0-value is the lowest [2]. The tendency for the activation energy to decrease near the phase transition temperature is also observed, which can be explained by a reduction in the number of degrees of freedom for the water molecule
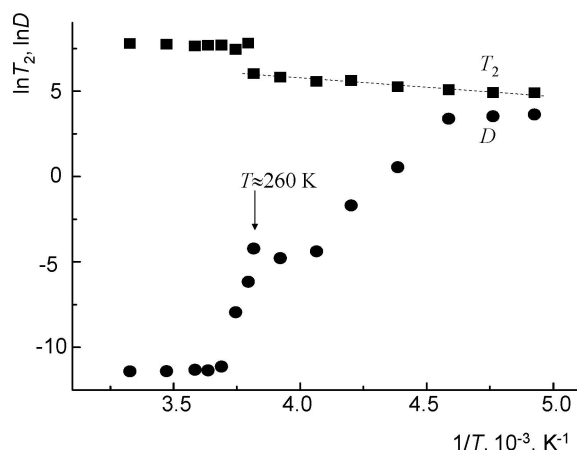
Fig. 3. Temperature dependences of the spin-spin relaxation time of water, T_2, and the self-diffusion coefficient of water, D, in MPS-250 silica gel pores

Fig. 4. Temperature dependence of the spin-spin relaxation time of water, T_2, in KSK-2 silica gel pores

motion at low temperatures under the confined geometry of pores.

Note that the results of NMR researches of rank A coals at low temperatures confirm the regularities in the behavior of the dynamic characteristics of water molecules obtained for other porous media [12, 13].

To explain the regularities demonstrated by water in anthracite pores, we used the same techniques applied to anthracite and discussed above to study water-saturated silica gel specimens with various pore diameters. In general, silica gels with narrow peaks in the pore dimension distribution are characterized by a phase transition temperature that is well pronounced in the temperature dependence of T_2 plotted in the Arrhenius coordinates. Such a behavior is different from that observed for water in anthracite pores, when the broadening of the absorption line (or a reduction of the relaxation time T_2) takes place in rather a wide temperature interval.

In Fig. 3, the examples of temperature dependences of the spin-spin relaxation time T_2 and the self-diffusion coefficient D for water in MPS-250 silica gel pores (the average pore size is 26 nm, see Table 1) are depicted. These dependences reveal a well-pronounced phase transition at the temperature $T \approx 260$ K (denoted by an arrow), which corresponds to a drastic variation of the water molecule mobility. The energy of the phase transition of water molecules in this porous sorbent, according to the Uo–Fedin formula [11] equals $U_0 = 40.6$ kJ/mol. A similar behavior was observed for water in pores of MSA-750 silica gel with a larger pore dimension. Water in silica gels with large pores (MPS-250 (26 nm) and MSA-750 (38 nm)) can be clearly resolved into two components: free water and water sorbed onto the active centers on
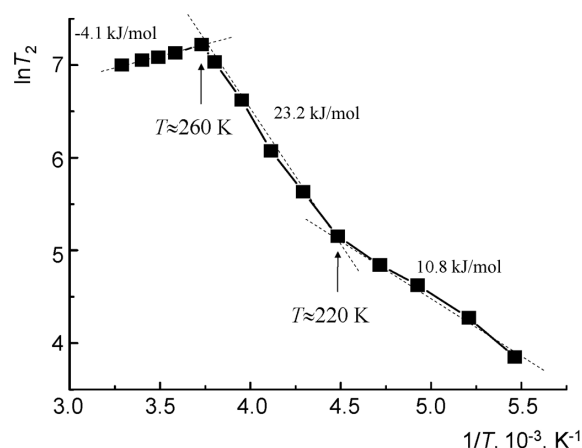
the pore surface. Some properties of water in pores can be explained by the exchange between those two components, which are characterized by different molecular mobilities [14].

Interesting modifications in the dynamics of water ^{1}H protons were observed in pores of KSK-2 silica gel, the dimension of which was smaller than 6.5 nm (Fig. 4). Three linear sections with different activation energies can be distinguished in the temperature dependence of the spin-spin relaxation time of water T_2 plotted in the Arrhenius coordinates: $E_a = -4.1$ kJ/mol in the high-temperature section $T > 260$ K, $E_a = 23.2$ kJ/mol in the range of 222 K $< T <$ 270 K, and $E_a = 10.8$ kJ/mol in the low-temperature interval 182 K $< T <$ 222 K.

Similarly, two linear sections with different activation energies can be distinguished in the temperature dependence of the spin-spin relaxation time T_2 plotted in the Arrhenius coordinates for SK-5a silica gel with the smallest pore dimension of 0.5 nm: $E_a = -4.1$ kJ/mol in the high-temperature section $T > 230$ K (this value is close to that for bulk diffusion of water) and $E_a = 4.0$ kJ/mol at low temperatures. Hence, the translational mobility of water molecules decreases at lower temperatures, and the magnitude $E_a = 4.0$ kJ/mol corresponds to the rotational degrees of freedom of water molecules sorbed onto the pore surface. In SK-5a silica gel with the smallest pore size, the observable effects characterize the mobility of water under considerable geometrical confinements. In the volume of such micropores, the generation of water clusters is hampered, so that the properties of water molecules correspond to those of molecules sorbed into a monolayer on the surface.

In general, our research of model porous sorbents with different pore dimensions (Table 1) showed that
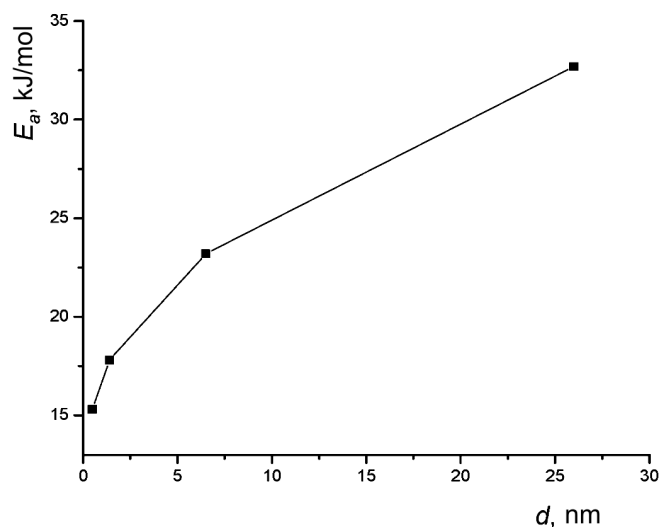
Fig. 5. Dependence of the activation energy E_a on the pore diameter d calculated from the Arrhenius dependences for the relaxation time T_2 of water in silica gel pores (Table 1)

the temperature, at which the mobility changes and the number of degrees of freedom for water molecule motion decreases, diminishes, if the pore diameter becomes smaller. In Fig. 5, the dependence of the activation energy E_a for T_2 on the pore diameter d in the low-temperature section of the phase transition is exhibited. Note that the quantity E_a grows with the parameter d, and such a behavior correlates well with a similar dependence of the phase transition energy U_0 for water in pores of coal specimens characterized by different metamorphism stages [2, 15].

4. Conclusions

The results of our NMR spectroscopy researches of water in anthracite pores in the temperature range from 90 K to room one revealed a drastic change of the water molecule mobility. An abnormal, non-Arrhenius temperature behavior of the self-diffusion coefficients was observed. Such a behavior can be explained by the features in the temperature dependences of bulk- and surface-transport contributions to the water diffusion in anthracite micropores. It was shown that, at low temperatures, the water molecules bound with active centers on the pore surface have one rotational degree of freedom with the activation energy close to $E_a = 4$ kJ/mol. We demonstrated the existence of a "smeared" phase transition for water in coal pores in the temperature range $T = 180 \div 230$ K. The energy of this phase transi-

tion was evaluated using the Uo–Fedin method to obtain $U_0 = 27 \div 35$ kJ/mol. The researches of model porous sorbents with narrow peaks in the distribution of pores over their dimensions showed that the phase transition of water in their pores is registered at a definite temperature, which decreases, as the pore diameter d diminishes. For the model sorbents, the activation energy E_a obtained from the Arrhenius dependences for the relaxation time T_2 grows with d, and this result correlates well with the dependence obtained earlier for the energy U_0 of the phase transition in water present pores of coal specimens at different metamorphism stages.

1. A.D. Alexeev, V.E. Zaidenvarg, V.V. Sinolitskii, and E.V. Ulyanova, *Radiophysics in Coal Industry* (Nedra, Moscow, 1992) (in Russian).

2. A.D. Alexeev, T.A. Vasilenko, and E.V. Ulyanova, Usp. Fiz. Nauk **175**, 1217 (2005).

3. G.Q. Zhang and G.J. Hirasaki, J. Magn. Res. **163**, 81 (2003).

4. T.A. Vasilenko, A.K. Kirillov, G.A. Troitsky, A.N. Molchanov, and G.P. Starikov, Fiz. Tekhn. Vysok. Davlen. **18**, N 2, 128 (2008).

5. A.A. Vashman and I.S. Pronin, *Nuclear Magnetic Relaxation Spectroscopy* (Energoatomizdat, Moscow, 1986) (in Russian).

6. A.D. Alexeev, G.P. Starikov, T.A. Vasilenko *et al.*, Visti Donetsk. Girnych. Inst. **1**, 174 (2005).

7. E. Lang and H.D. Lüdemann, J. Chem. Phys. **67**, 718 (1977).

8. J. Beau and W. Webber, Progr. Nucl. Magn. Res. Spectr. **56**, 78 (2010).

9. F. Mallamacea, M. Broccio, C. Corsaro *et al.*, J. Chem. Phys. **124**, 161102 (2006).

10. V.I. Roldugin, V.M. Zhdanov, and V.V. Volkov, Strukt. Dynam. Molek. Syst. N 4, 84 (2008).

11. J. Uo and E.I. Fedin, Fiz. Tverd. Tela **4**, 2233 (1962).

12. A. Faraone, L. Liu, C.J. Moi *et al.*, J. Chem. Phys. **121**, 10843 (2004).

13. V.I. Betekhtin, A.N. Bakhtibaev, E.A. Egorov *et al.*, Tsement, No. 10, 8 (1989).

14. G. Belfort and N. Sinai, in *Water in Polymers*, edited by S. P. Rowland (American Chemical Society, Washington, DC, 1980), p. 323.

15. A.D. Alexeev, T.A. Vasilenko, A.K. Kirillov, A.N. Molchanov, G.A. Troitsky, and A.V. Donchuk, Fiz. Tekhn. Vysok. Davlen. **20**, N 2, 133 (2010).

ВИВЧЕННЯ ТЕМПЕРАТУРНОЇ
ЗАЛЕЖНОСТІ ДИНАМІЧНИХ ПАРАМЕТРІВ
ВОДИ В ПОРОВОМУ ОБ'ЄМІ ВИКОПНОГО ВУГІЛЛЯ

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Р е з ю м е

Подано результати дослідження температурних залежностей часів релаксації T_1 і T_2 та коефіцієнта самодифузії води D у насичених вологою порах викопного вугілля (антрациту). Вимірювання проводили з застосуванням методів спін-ехо і ядерного магнітного резонансу (ЯМР) широких ліній. Резонансна частота для спінів ядер водню ^{1}H становила $f \approx 20$ МГц і температура T змінювалася в інтервалі від 90 K до кімнатної. Результати досліджень свідчать про наявність "розмазаного" фазового переходу, що спостерігається в інтервалі температур $T = 180$–230 K. Енергія цього фазового переходу, оцінена при використанні методу Уо–Федіна, становила $U_0 = 27$–35 кДж/моль. Показано, що енергія активації E_a, яка відповідає температурній залежності T_2, зростає при збільшенні T від 4 кДж/моль (90 K) до 18 кДж/моль (300 K). Спостерігалося відхилення температурної залежності коефіцієнта самодифузії D від ареніусової, що пояснюється переходом від об'ємної до поверхневої дифузії при зниженні температури.