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ANOMALOUS NEGATIVE THERMAL EXPANSION IN A CONDENSED HETEROGENEOUS LYOPHOBIC SYSTEM

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A reduction in the volume of a heterogeneous lyophobic system (HLS) at the temperature growth (the so-called negative thermal expansion, NTE) is experimentally observed. For the investigated HLS “silicalite-1 + water”, the NTE effect is shown to exceed the corresponding values observed for other known materials by more than an order of magnitude. The physical principles of this phenomenon are explained, and a mathematical model for its description is proposed.

Keywords: phase interface, porous body, PV-isotherm, intrusion/extrusion, simulation, experiment.

1. Introduction

The phenomenon of negative thermal expansion is a process, in which the volume of a body diminishes, as its temperature increases [1–7]. This phenomenon can be classified as abnormal, because the overwhelming majority of substances and systems are characterized by positive thermal expansion coefficients (TECs) [6, 7]. Only such rare representatives as the family of cubic zirconium tungstate ZrW_2O_8 [5], the family of AM_2O_7 compounds, where $A = U, Th, Zr, Hf, Sn$ and $M = P, V$ [3], and some zeolite and zeolite-like compounds [4] reduce their volume when the temperature increases in a certain interval. This phenomenon is used for the solution of some technical problems [7] in such domains as materials science, electronics, medicine, photonics, and others. The most important of those problems is the creation of composite materials with a required (given) TEC. This task is solved by combining materials with positive and negative TECs. An illustrative partial case of the problem concerned is the creation of a material with the zero TEC: the practical importance of

a substance, whose dimensions remain insensitive to the temperature, is evident.

Bearing the practical applicability of indicated materials in mind, their major characteristics are the degree of material volume, V , reduction as the temperature, T , changes, i.e. the quantity $\frac{dV}{dT}$, and its temperature dependence. A negative value of TEC is one of the unusual properties of heterogeneous lyophobic systems (HLSs) [2]. In this article, we continue to develop ideas concerning the negative thermal expansion in a wide class of HLS by attracting new experimental data and theoretical viewpoints. Physical mechanisms, which this phenomenon is based on, are explained. They allow the value of derivative $\frac{dV}{dT}$ to be considerably increased and the character of its temperature dependence to be changed in comparison with those for known materials with the negative TEC.

2. Theoretical Foundations

The heterogeneous lyophobic system or the repulsive clathrate (RC) [2, 8–10] is a condensed system consisting of a capillary-porous solid and a liquid that does not wet the former (the contact wetting angle $\theta \gg 90^\circ$). Such thermomechanical systems have a number of physical properties, which allows them

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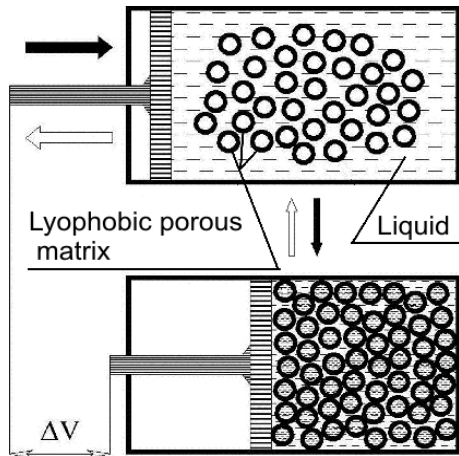


Fig. 1. Example of the physical model of repulsive clathrate

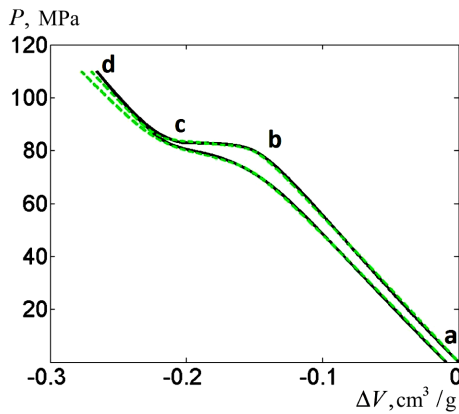


Fig. 2. PV-isotherm (at 323 K) of the “mechanical” compression/expansion of repulsive clathrate on the basis of silicalite-1 and water. The solid and dashed curves demonstrate, respectively, the experimental data and the results of model calculations according to Eq. (6)

to be used – although nonconventionally, but effectively – for the accumulation of thermal and mechanical energy [11–13], for the dissipation of the latter [10, 14–18], and for the transformation of thermal energy into mechanical one and *vice versa* [19, 20]. The physical model of the HLS/RC system is explained in Fig. 1. A capillary-porous body (a matrix, which is usually a powder of porous particles [11–13, 16–18] or, more seldom, a monolithic framework [21]) and a liquid that does not wet this body ((the contact wetting angle $\theta \gg 90^\circ$) are placed into a working chamber of the “cylinder–piston” type. The lyophobic character of the system prohibits the liquid from an unal-

lowed penetration into the energy unprofitable space of the porous matrix. For the liquid to penetrate into the pores/capillaries (the process of forced intrusion), it must overcome a potential barrier, which is determined by the Laplace capillary pressure written down in the Washburn form as follows [22]:

$$P^{\text{int,ext}} = \frac{\sigma |\cos \theta^{\text{int,ext}}|}{kr} \quad (1)$$

Formula (1) testifies that the coefficient of liquid surface tension σ , the intrusion contact angle $\theta^{\text{int}} \gg 90^\circ$, the pore radius r , and the geometry of the matrix pore space (the factor $0.33 < k < 0.5$) influences the magnitude of pressure P^{int} that should be applied to the system for the intrusion (the subscript “int”) of the liquid into matrix pores to take place. Of course, for Eq. (1) to be able to describe nano-capillary HLSs, corrections related to a considerable curvature of the tension surface must be introduced into it.

The intrusion process is accompanied by a reduction in the volume of heterogeneous system by the volume of matrix pores ($\Delta V = V_{\text{pore}}$) and a development of the interphase surface Ω at the solid–liquid interface, with the accumulation of the Gibbs free energy in the system, $G = \sigma \Omega \cos \theta$. Afterward, this energy can be released, partially or almost completely, for executing a useful mechanical work. We adopt that the hysteresis of the wetting contact angle, $\Delta \theta$ (the difference between the intrusion, θ^{int} , and extrusion, θ^{ext} , contact angles), governs the magnitude of pressure hysteresis, $H = P^{\text{int}} - P^{\text{ext}}$; the quantity P^{ext} is the pressure of a free liquid outflow from the matrix pore space. The hysteresis H defines the functional capability of RC; namely, if H is small ($P^{\text{int}} \approx P^{\text{ext}}$), the system is expedient to be used for the accumulation or transformation of energy in thermomechanical systems, and, at large H ($P^{\text{int}} \gg P^{\text{ext}}$), for its dissipation.

A typical PV-isotherm of HLS (the dependence of the system volume V on the pressure P applied to the system) is shown in Fig. 2. It has three characteristic sections. At a preliminary compression stage (section a-b), the increase of the pressure in the system ($P < P^{\text{int}}$) changes the system volume slightly (here, we have the elastic deformation of the liquid and the empty porous matrix). In the section b-c (at $P = P^{\text{int}}$), the intrusion of the liquid into the matrix pores takes place, which is accompanied by a substantial reduction in the HLS/RC volume. For

real matrices, there always exists a certain deviation of pore dimensions from the average value r , i.e. the pore size dispersion D_r , which induces the dispersion of values for the intrusion and extrusion pressures. A further growth of the pressure ($P > P^{\text{int}}$, section c-d) results in an insignificant change of the condensed system volume (the elastic deformation of the liquid and the filled porous matrix, which is somewhat smaller in comparison with that in the first section). The inverse process (section d-a) takes place for the process of free extrusion (Fig. 2). The compression/expansion PV -isotherm is a key characteristic of repulsive clathrate, being determined by the properties of the liquid, geometry of the pore space (including the size distribution of pore radii), and the phobicity of the system.

The application of HLS/RC with a large hysteresis H allows the mechanical energy with a power of 40–50 W/cm³ to be effectively dissipated at frequencies higher than 20 Hz [15, 23], which are inaccessible for ordinary hydraulic shock-absorbers. A high stability of the operation characteristics for such HLS/RCs after 10⁶–10⁷ cycles of complete compression/decompression was demonstrated [17]. A typical value of dissipated energy in a cyclic process amounts to about 12 J per gram of the matrix mass [16]; the corresponding values for the irreversible regime (e.g., for a special bumper) acquire magnitudes up to 41 J/g [18]. Accumulation of mechanical energy with the help of the system “super-hydrophobic zeolite + water” is characterized by values up to 15 J/g, and 97% of this energy can be released to execute a useful work [13]. The phenomenon of abnormal dilatometry for one class of HLSs [24] found its application in the nuclear power engineering [25].

3. Experimental Part

3.1. Materials

In this work, we used repulsive clathrates “super-hydrophobic silicalite-1 + water”. Silicalite-1 is a zeolite with the MFI-structure. It is naturally super-hydrophobic. The average radius of its pores $r \approx 3$ nm, the specific interphase surface $\Omega \approx 400$ m²/g, and the specific pore volume $V_{\text{pore}} \approx 0.12$ cm³/g. By its energy parameters – a high accumulated specific energy at a small hysteresis $H = P^{\text{int}} - P^{\text{ext}}$ – the used RC (silicalite-1 + water) is not a “champion” among the available and studied materials [11–13]. However, owing to its simple topology (the pore

space in silicalite-1 is composed of independent parallel cylinders), this material is a good example of super-hydrophobic capillary-porous matrices for the creation of repulsive clathrates. It makes the research of main clathrate characteristics and the phenomena occurring in clathrates simpler, including the verification of HLS/RC mathematical models. In this work, we used a commercial variant of silicalite-1 (Aldrich) synthesized following the standard procedure in the presence of fluorine ions.

3.2. Experimental equipment and the procedure of specimen fabrication

To obtain the diagram of the temperature-, $V(T)$, or pressure-induced, $V(P)$, volume change in the course of the RC heating/cooling or compression/expansion, respectively, cycle, we used a scanning transitiometer ST-7M, a highly baric ergo-calorimeter developed and modernized by Prof. S.L. Randzio at the design department and the plant of scientific equipment of the Institute of Physical Chemistry (the Polish Academy of Sciences) according to the idea and technical documentation of Prof. V.A. Eroshenko (the NTUU “Kyiv Polytechnical Institute”). Unlike the basic ST-7 unit [26–28], high-precision induction volumeters on the basis of metal sylphon bellows were mounted in the high-pressure measuring chambers (up to 200 MPa) of the ST-7M unit.

The scheme of the experimental installation is depicted in Fig. 3, *a*. One can see that the open ends of sylphon bellows are rigidly attached to the cylindrical section of measuring chambers (the test sample is placed into one of them and the reference sample into another one); their other ends are connected to metal non-magnetic rods with crimped magnetic cores (armatures) of induction sensors. The windings of the latter are located beyond the hydraulic chamber manufactured of a non-magnetic material. The axial shift of sylphon bellows (with a constant effective cross-section) characterizes the volume variation during the processes of RC compression/expansion or heating/cooling. This shift is registered by linear variable differential transformers (LVDT-sensors) [29]. The readout of the signal from the LVDT-sensors calibrated in volume units can be done in the ST-7M unit both in parallel and differentially.

The pressure in the measuring chambers is provided with the help of a high-pressure pump driven by a step motor. In the case of the basic ST-7 unit

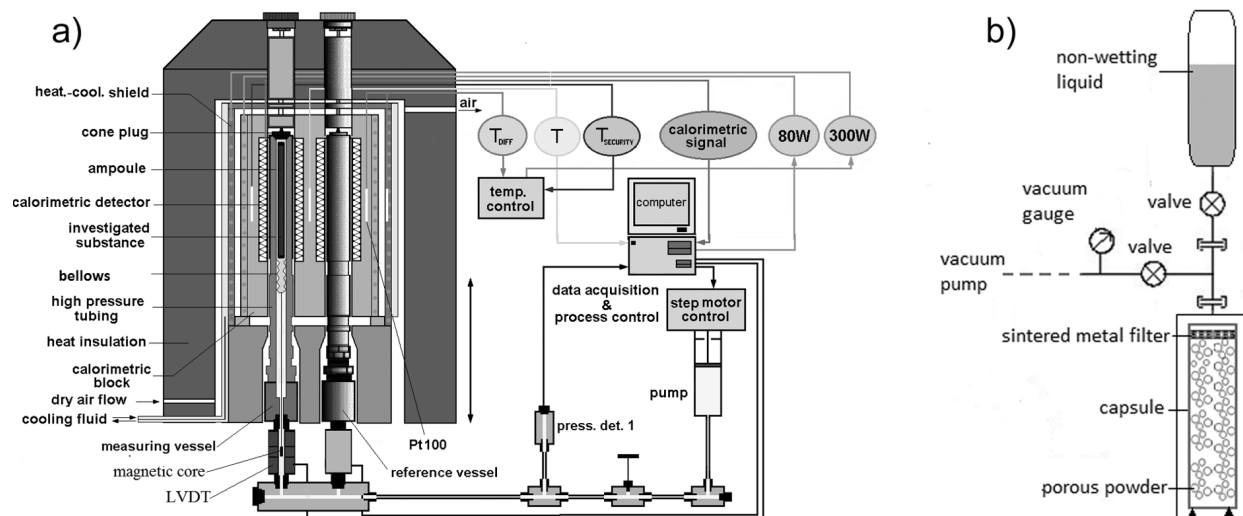


Fig. 3. Experimental installation for measuring $V(P)$ - and $V(T)$ -diagrams with the simultaneous registration of thermal effects (a); Schematic diagram of a stand for the specimen fabrication (b)

version, the number of steps (the number of separate doses) was used to evaluate the volume change during the processes of compression/expansion or heating/cooling of the system. Possible failures in the course of operation of a step motor and a counter device gave rise to considerable errors in the determination of volume change, while measuring the $V(P)$ -isotherms. In the modified construction (the ST-7M unit), the assembly “step motor–pump” was retained, but it played a second-order role. Real volume changes in the studied system were evaluated according to the readings of an induction volumeter, which made the metrological characteristics of the ST-7M unit much better. A high determination accuracy of thermal effects and reading out the PV -isotherms were achieved owing to the application of an automatic temperature control system on the basis of a proportional-integral-derivative (PID) controller. The readout of a pressure signal in the hydrosystem was carried out with the help of a pressure transducer built into the hydraulic pipe connecting the pump and the measuring chambers.

The ST-7M unit can operate in various regimes [26–28]. In this work, we simultaneously registered a variation of the specimen volume as a result of the compression/expansion, heating/cooling, or pressure growth in the chambers. As a rule, the rate of compression/expansion in the experiments of the type “forced mechanical intrusion–free extrusion”

amounted to 10^{-3} MPa/s. In the experiments with the “thermal” intrusion/extrusion, the rates of heating and cooling were 4×10^{-3} K/s. In both cases, the low rate was needed to ensure the quasistatic character of the processes of “mechanical” and “thermal” intrusion of the liquid into matrix pores. The accuracy of measurements in both experiments was checked with respect to three thermodynamic parameters: ± 0.15 MPa for the pressure, $\pm 3.3 \times 10^{-4}$ cm³ for the volume, and ± 0.01 K for the temperature.

In Fig. 3, b, a simplified scheme of the specimen preparation is shown. The weighed amount of silicalite-1 was inserted into a metallic capsule and closed by a ceramic-metal porous cover. The porous matrix mass in a capsule was approximately equal to 2 g. The capsule with the matrix was carefully degassed for 2 to 4 h until a pressure of about 10^{-2} mbar was attained. After degassing, the capsule with the matrix was filled with distilled preliminarily degassed water through the porous cover. The capsule was filled with water under vacuum to ensure the effective filling of the space between porous particles of the hydrophobic matrix with water (the procedure of RC fabrication). When the calorimeter body was in the extreme upper position (Fig. 3, a), the capsule with RC and the capsule with water were put into the measuring and compensation, respectively, high-pressure chambers, which were preliminary filled with degassed distillate. When embedding the capsules,

excess water was freely displaced from the chambers through their input holes, which excluded the ingress of air into the chamber. Afterward, the chambers were tightly closed using special screw covers, and the calorimeter body with two reception channels acting on the thermal detectors was carefully put down on both measuring chambers. The sliding fit of chambers in the calorimeter channels provided an effective heat exchange between the measuring chambers and the thermal detectors.

3.3. Experimental procedure

The compression/expansion $P(V)$ -isotherms were registered automatically. A specimen (repulsive clathrate) prepared as was described above and arranged in the working chamber was undergone an external pressure that grew linearly in time at the rate $\frac{dP}{dt} = 10^{-3}$ MPa/s from the initial value to $P_{\max} \approx 110$ MPa. Then the pressure was lowered down at the same rate to the initial value. During the whole experiment, the temperature was maintained constant by an automated system on the basis of a PID-controller.

While registering the $V(T)$ -dependences, the initial pressure $P = 80.5$ MPa was created in the working chamber. Then the cycle of heating/cooling was executed in the interval from $T_{\min} = 283$ K to $T_{\max} = 313$ K at the rate $\frac{dT}{dt} = 4 \times 10^{-3}$ K/s.

3.4. Experimental results and their discussion

In Fig. 4, the temperature dependence of the volume of RC created on the basis of “silicalite-1 + water”, which was measured provided a constant loading on the system (the initial pressure in the system amounted to $P = 80.5$ MPa), is depicted (the solid curve). The plot of the thermal cycle testifies that the increase of the temperature from its initial value $T = 283$ K to the temperature $T \approx 303$ K does give rise to substantial variations in the system volume. If the temperature grows further, $T > 303$ K, a linear reduction of the specific volume of the system is observed, which is associated with the water intrusion into the pores of silicalite-1. In particular, in the course of intrusion, the coefficient of negative thermal expansion for the investigated system at the stage of the matrix filling was equal to $\beta = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_{P_{\text{int}}} = -5.7 \times 10^{-3} \text{ K}^{-1}$.

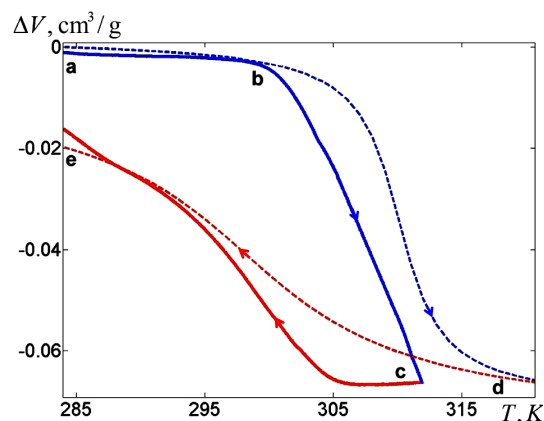


Fig. 4. Cycle of “thermal” intrusion/extrusion for RC on the basis of silicalite-1 and water at the initial pressure $P_0 = 80.5$ MPa. The solid curve corresponds to experimental data, the dashed one to the results of model calculations

Let us compare the result obtained with the corresponding data for known materials with a negative TEC. In most cases, the relevant magnitudes are of the order of -10^{-5} K^{-1} [3–7]. For instance, the phenomenon of negative thermal expansion recently described for cubic ScF_3 is characterized by $\beta = -1 \times 10^{-5} \text{ K}^{-1}$ [30], and the value $\beta = -9 \times 10^{-5} \text{ K}^{-1}$ was obtained for a $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_2\text{As}_2$ specimen [31]. Those parameters were considered to be anomalously high and attracted a substantial theoretical interest in the scientific community [32, 33].

Hence, the value of TEC for the HLS on the basis of “silicalite-1 + water” is considerably larger than the corresponding values for known materials. Namely, the actual record results are exceeded by more than an order of magnitude. It should be noted that the result obtained for the examined HLS was observed in a rather narrow temperature interval, which is not true for $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_2\text{As}_2$ and ScF_3 materials. However, as will be shown below, the temperature range, in which TEC is negative, can be considerably extended by combining various capillary-porous matrices into a single HLS.

As the temperature decreases, the volume of the system “silicalite-1 + water” increases. This process has a hysteresis in the temperature interval of “thermal” intrusion and extrusion (Fig. 4): when the system is cooled down to the initial temperature, its volume is somewhat smaller (point e) than the initial value (point a). In view of the existence of a hysteresis in the isothermal process of compression/expansion

sion/expansion of RC with the intrusion/extrusion with respect to the pressure (Fig. 2), this result seems quite expectable. Of course, a hysteresis in the cycle of HLS heating/cooling can be regarded as an undesirable phenomena in this case. However, as was mentioned above, the system “silicalite-1 + water” is a good model example, whereas HLSs with the minimal hysteresis are more expedient to be used for practical purposes. A number of zeolites, which were studied experimentally with respect to their interaction with water [11–13], satisfy this condition; namely, they have a small hysteresis magnitude with respect to the parameter “pressure” (less than 3%) and a high stability of their properties. The difference between the inflow and outflow behaviors of the liquid in the course of the isothermal “mechanical” cycle (Fig. 2) and the origins of its emergence were studied in work [34]. In particular, it was demonstrated that this difference is a result of silanol defects on the internal matrix surfaces and can be eliminated by synthesizing the high-quality matrices.

4. Theoretical Analysis

The reported experiments were carried out in a regime that can be characterized as quasistatic. Therefore, it is expedient to apply the apparatus of equilibrium thermodynamics to the interpretation of the results. In work [34], it was shown that the equation

$$\Delta V^{\text{int,ext}} = V_0 - V = f^{\text{int,ext}}(P) + \kappa_T^{V_0} P + C \quad (2)$$

can be used for simulating the compression/expansion PV -isotherms. Here, ΔV is a change of the RC volume (the superscript “int” stands for intrusion, and “ext” for extrusion); V_0 is the initial volume of a working substance consisting of the initial liquid volume V_p and the empty matrix V_m ($V_0 = V_p + V_m$); the term with the coefficient $\kappa_T^{V_0} = \left(\frac{\partial V_0}{\partial P}\right)_T$ determines the isothermal elastic deformation of bulk RC components under the pressure P ; C is the integration constant determined from the initial condition $[\Delta V^{\text{int,ext}}]_{P_0} = 0$, where P_0 is the initial pressure in the system; and the function $f^{\text{int,ext}}(P)$ describes a change of the RC volume owing to the intrusion/extrusion of the liquid into the pore space of the matrix. Since the dependence of the degree of filling of the pore space on the pressure applied to the system is governed by the distribution of matrix

pore radii (the relation between the pressure and the radius of filled pores is determined by Eq. (1)), it is convenient to use the distribution functions from probability theory for the functions $f^{\text{int,ext}}(P)$. For example, if the matrix pores are characterized by a certain dominating average radius, and symmetric deviations from this average value are insignificant, it is expedient to use the Cauchy distribution function [35],

$$f^{\text{int,ext}}(P) = \frac{V_{\text{pore}}}{\pi} \arctan\left(\frac{P - P^{\text{int,ext}}}{D^{\text{int,ext}}}\right) \quad (3)$$

or the Gauss distribution [35],

$$f^{\text{int,ext}}(P) = \frac{V_{\text{pore}}}{2} \operatorname{erf}\left(\frac{P - P^{\text{int,ext}}}{\sqrt{2}D^{\text{int,ext}}}\right), \quad (4)$$

where the error function is defined by the formula

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \quad (5)$$

The volume of the pore space V_{pore} , the average pressures $P^{\text{int,ext}}$ inducing the intrusion/extrusion, and their dispersions $D^{\text{int,ext}}$ can be determined from the passport characteristic of the matrix. For this purpose, the distribution functions of pore volumes over pore radii and Eq. (1) are used. This is a procedure that is inverse to what is applied in the practice of mercury [36] and water [37] porosimetries. If the distribution of pore radii is more complicated—for example, it is asymmetric—the corresponding functions from probability theory, such as Weibull, log-normal, and others [35], or their combination (if that or another RC is synthesized on the basis of several matrices combined into a single RC) can be used. For instance, let us use the values $P^{\text{int}} = 82.85$ MPa, $P^{\text{ext}} = 78.63$ MPa, $D^{\text{int}} = 0.9$ MPa, $D^{\text{ext}} = 3.5$ MPa, $V_{\text{pore}}^{\text{int}} = 0.073$ cm³/g, $V_{\text{pore}}^{\text{ext}} = 0.068$ cm³/g (the inequality $V_{\text{pore}}^{\text{ext}} < V_{\text{pore}}^{\text{int}}$ means that not all the liquid left the matrix), and $\kappa_T^{V_0} = -1.8 \times 10^{-3}$ cm³/MPa/g, and the Cauchy distribution function [35] to plot the model curves for the compression/expansion PV -isotherms according to Eq. (3) and compare them with the experimental result (Fig. 2),

$$\begin{aligned} \Delta V^{\text{int,ext}} &= V_0 - V = \\ &= \frac{V_{\text{pore}}^{\text{int,ext}}}{\pi} \arctan\left(\frac{P - P^{\text{int,ext}}}{D^{\text{int,ext}}}\right) + \kappa_T^{V_0} P + C. \end{aligned} \quad (6)$$

The applicability of Eq. (6) to the description of isothermal processes and the simulation of “unordinary” thermal effects (the endothermic effect of RC compression and the exothermic effect of RC expansion) [34] allows us to suppose that an equation of type (2) can be proposed as an equation of the HLS state, because it describes a relation of the basic macroscopic parameters in the thermodynamic system: the pressure P , the volume V , and the temperature T (through the unambiguous relation of the temperature to the liquid surface tension σ and, therefore, to the intrusion/extrusion pressures by means of Eq. (1)). However, the equation of state must be verified not only for the isothermal process, but for other processes—isochoric, isobaric, adiabatic, and so on—as well. In this work, the equation is verified with the use of a non-standard process, which is more complicated in comparison with the processes mentioned above, but is more adequate to the practical application of HLS; this is the process with a constant constraint.

In this process, RC undergoes the action of a constant force, which is not enough for the liquid to penetrate into the matrix pores at the initial temperature. The temperature growth with respect to the initial one (which is given beforehand) gives rise to two effects. First, the pressure in the system increases owing to the thermal expansion of its bulk components (the liquid and the matrix). Second, the coefficient of liquid surface tension decreases. Both those effects result in that, at a certain characteristic temperature, the pressure in the system becomes equal to the Laplace capillary pressure at the specified temperature. As a result, the liquid fills the matrix capillaries, and the RC volume diminishes (Fig. 4).

To describe this process, Eq. (3) must make allowance for the temperature dependence of the intrusion/extrusion pressures $P^{\text{int,ext}}$ and a change of the pressure in the system $P(T)$ occurring due to the thermally induced deformation of the liquid and the matrix. As a rule, the both dependences are linear [38, 39]. According to Eq. (1), the quantities $P^{\text{int,ext}}$ are determined by the temperature dependences of the surface tension coefficient σ and the wetting contact angle θ . For some systems—in particular, for the system “silicalite-1 + water” [38] — the temperature dependence of the contact angle can be neglected (of course, this is a certain approximation). Using

Eq. (1), the following equation can be written down:

$$P^{\text{int,ext}}(T) = \frac{d\sigma}{dT} \frac{P(T_0)}{\sigma(T_0)} (T - T_0) + P(T_0). \quad (7)$$

It is well-known that the liquid surface tension considerably changes if the liquid surface becomes substantially curved, and this phenomenon undoubtedly does take place in nano-sized capillaries. This variation is usually taken into account by using the Gibbs–Tolman–Koenig–Buff (GTKB) equation [40],

$$\sigma = \sigma_\infty \left(1 + 2\frac{\delta}{r}\right)^{-1}, \quad (8)$$

where σ_∞ is the surface tension of a flat surface, and δ is the Tolman length. In his work [40], R. Tolman derived the GTKB equation, by using the approximation $\delta = \text{const}$, which enables us to use the transformation

$$\frac{d\sigma}{dT} \frac{1}{\sigma(T_0)} = \frac{d\sigma_\infty}{dT} \frac{1}{\sigma_\infty(T_0)} \quad (9)$$

in Eq. (4) and, hence, to avoid the determination of the Tolman length in the analysis to follow.

The pressure change in the system, $P(T)$, is determined by means of the isochoric coefficient for the pressure in the liquid and the matrix, $\left(\frac{\partial P}{\partial T}\right)_V$. Using Eq. (7) and the classical relation between the thermal coefficients for simple systems [39]

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V, \quad (10)$$

let us rewrite Eq. (6) in the form

$$\Delta V^{\text{int,ext}} = V_0 - V = \frac{V_{\text{pore}}^{\text{int,ext}}}{\pi} \times \arctan \left(\frac{P(T) - P^{\text{int,ext}}(T)}{D^{\text{int,ext}}} \right) + \left(\frac{\partial V}{\partial T}\right)_P T + C_2. \quad (11)$$

Here, the constant C is determined from the condition $[\Delta V^{\text{int,ext}}]_{T_0} = 0$, and the term $\left(\frac{\partial V}{\partial T}\right)_P T$ is responsible for the temperature dependence of variations of the volume (the expansion and the reduction of system’s bulk components, the liquid and the matrix). In view of the conditions, under which the experiment dealing with “thermal” intrusion/extrusion was carried out, this effect could not bring about the volume change, because the system undergone the action of a

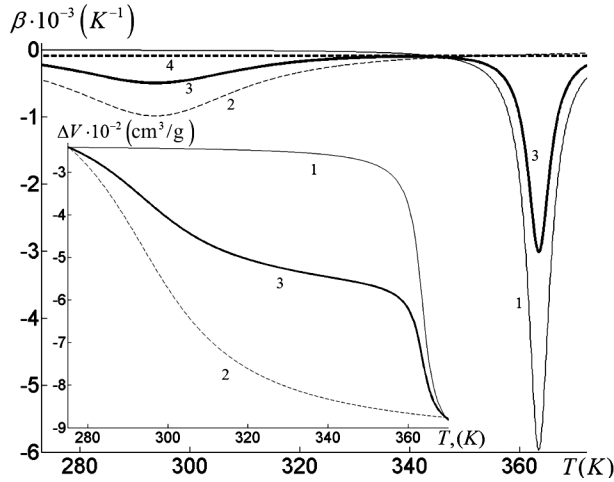


Fig. 5. Thermal expansion coefficient for HLSs on the basis of water + silicalite-1 (1), water + zeolite SSZ (2), their combination “water + 2 matrices”(3), and for a $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_2\text{As}_2$ specimen (4) (work [31]). The inset demonstrates the behavior of variations of the volume, as the temperature grows

constant loading (the initial pressure P_0). Nevertheless, those conditions gave rise to the pressure growth in the system at its heating (and to the pressure drop at cooling) owing to the isochoric heating/cooling of the system to the intrusion/extrusion temperature. Hence, while comparing the model curve plotted in accordance with Eq. (11) and the experimental one, the terms $(\frac{\partial V}{\partial T})_P T$ can be neglected, and the pressure growth can be taken into consideration in the form

$$P(T) = \left(\frac{\partial P}{\partial T}\right)_V (T - T_0) + P(T_0). \quad (12)$$

Using the values [39] $T_0 = 283 \text{ K}$, $P_0 = 80.5 \text{ MPa}$, $\frac{d\sigma_\infty}{dT} = -1.6 \times 10^{-4} \text{ J/m}^2/\text{K}$, $\sigma_\infty(T_0) = 74.31 \times 10^{-3} \text{ J/m}^2$, $\frac{1}{V_0} (\frac{\partial V}{\partial T})_P = 3 \times 10^{-4} \text{ K}^{-1}$, and $\frac{1}{P_0} (\frac{\partial P}{\partial T})_V = 2.2 \times 10^{-3} \text{ K}^{-1}$ and making allowance for the remarks made above, let us compare the theoretical curve of “thermal” intrusion/extrusion plotted in accordance with Eq. (11) and the corresponding experimental dependence (Fig. 4). One can see that Eq. (11) satisfactorily approximates experimental results (the theoretical curve is shifted with respect to the experimental one by about 4 K). A difference between the behavior of the liquid inflow/outflow during the heating/cooling of the system is also observed: the dispersion of the theoretical curve is smaller than that of the experimental

one. This difference is expectable, because the dependence $P(T)$, which is used in Eq. (11), does not consider the change in the volume owing to the gradual penetration/exit of the liquid into/from the pore matrix space. This means that, within the intrusion/extrusion interval, the temperature dependence of the pressure, $P(T)$, is less considerable. Nevertheless, the application of basic thermodynamic analysis gave satisfactory theoretical results, which can be improved by considering the features of a real thermomechanic system.

Note that, if an HLS/RC system combined of n different matrices is used, the first term in Eq. (2) reads

$$f(P) = \sum_i^n f_i(P), \quad (13)$$

where the function f_i demonstrates the dependence of the pressure on the pore distribution in the i -th matrix. Let us illustrate this trick by plotting the theoretical temperature dependence of TEC β in Fig. 5 (the derivative of Eq. (2) with respect to the temperature) and the “thermal” intrusion/extrusions $V(T)$ (Eq. (11)) for a heterogeneous system on the basis of water and silicalite-1 (this system is studied experimentally in this work) and for zeolite of the SST type with the use of the experimental PV -isotherm for the latter [13]. Let us also compare the same dependences of TEC β for the $\text{Ca}_{0.8}\text{La}_{0.2}\text{Fe}_2\text{As}_2$ specimen taken from work [31].

One can see from Fig. 5 that the required temperature dependence of the thermal expansion coefficient for HLS/RC can be obtained by varying the number and the kinds of capillary-porous matrices in the course of synthesis of a required heterogeneous system. There is a logic dependence between the TEC value and the temperature interval length, where this dependence holds: the smaller the dispersion of pore radii in the matrix, the larger is the TEC value and the narrower is the working temperature range (and *vice versa*). The maximum obtained TEC values were $\beta = -10^{-3} \text{ K}^{-1}$ for HLS/RC on the basis of water and zeolite of the SSZ type and $\beta = -5.7 \times 10^{-3} \text{ K}^{-1}$ for the HLS on the basis of silicalite-1. Those values exceed the TEC values for known materials by more than an order of magnitude [3–7, 30, 31]. While fabricating HLSs by combining the matrices specified above and taking them in the equal volume ratio, the

temperature interval where the TEC had considerable negative values was extended to about 100 K.

The adequacy of Eq. (2) for the description of isothermal processes [34] and the processes running at a constant loading, which are considered in this work, is a sound argument for its application as the equation of state for heterogeneous lyophobic systems. This is an extremely important factor for the possibility of a comprehensive thermodynamic analysis of the system. Equation (2) must also be verified, using the experimental results obtained under isobaric, isochoric, adiabatic, and other conditions. This verification, as well as experiments where the HLS/RCs with the minimal hysteresis H are used, will be the subject of following publications.

5. Conclusions

To summarize, the phenomenon of negative thermal expansion and the origins of its anomalous value for heterogeneous lyophobic systems, repulsive clathrates, has been studied experimentally and theoretically. The following main results were obtained.

1. It was experimentally shown for the first time that the coefficient of negative thermal expansion for the HLS/RC system can be larger by more than an order of magnitude than the corresponding values for known materials [3–7, 30, 31].

2. A physico-mathematical model of HLS/RC was proposed which takes into account the phenomenon of negative TEC and allows its value to be obtained proceeding from the parameters of the liquid and the matrix (or the combination of matrices). The theoretical approximation correlates well with the results calculated from experimentally obtained compression/expansion PV -isotherms of examined HLS/RCs.

3. On the basis of experimental data concerning the “thermal” intrusion/extrusion of the liquid in HLS/RC at a constant hydrostatic loading on the system, the equation of its state (Eq. (2)) was substantiated and verified.

4. A possibility of creating HLS/RCs with required negative TECs by combining several matrices into a single HLS/RC is indicated. Such systems can be prepared in the form of suspensions or colloid solutions.

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1. C.V. Raman and T.M.K. Nedungadi, *Nature* **145**, 147 (1940).
2. V.A. Eroshenko, *Dokl. Akad. Nauk Ukr. SSR Ser. A*, No. 10, 79 (1990).
3. V. Korthuis, N. Khosrovani, A.W. Sleight, N. Roberts, R. Dupree, and W.W. Warren, *Chem. Mater.* **7**, 412 (1995).
4. P. Tschaufeser and S.C. Parker, *J. Phys. Chem.* **99**, 10609 (1995).
5. J.S.O. Evans, T.A. Mary, T. Vogt, M.A. Subramanian, and A.W. Sleight, *Chem. Mater.* **8**, 2809 (1996).
6. J.S.O. Evans, *J. Chem. Soc. Dalton Trans.* **19**, 3317 (1999).
7. G.D. Barrera, J.A.O. Bruno, T.H.K. Barron, and N.L. Allan, *J. Phys. Condens. Matter* **17**, 217 (2005).
8. V.A. Eroshenko, in *Capillary Properties and Adhesion of Alloys* (Naukova Dumka, Kyiv, 1987), p. 100 (in Russian).
9. V.A. Eroshenko, *Promyshl. Teplotekhn.* **14**, 22 (1992).
10. V.A. Eroshenko and Yu.F. Lazarev, *Prikl. Mech. Tekhn. Fiz.* **53**, 98 (2012).
11. V. Eroshenko, R.-C. Regis, M. Soulard, and J. Patarin, *J. Amer. Chem. Soc.* **123**, 8129 (2001).
12. V. Eroshenko, R.-C. Regis, M. Soulard, and J. Patarin, *C.R. Acad. Sci. Ser. B* **3**, 111 (2002).
13. L. Tzanis, M. Trzpit, M. Soulard, and J. Patarin, *J. Phys. Chem. C* **116**, 20389 (2012).
14. V.A. Eroshenko, Patent France WO 01/55616 A1, F 16 F 9/00.
15. V.A. Eroshenko, I.I. Piatiletov, L. Coiffard, and V.P. Stoudenets, *Proc. Mech. Eng. D* **221**, 301 (2007).
16. C.V. Suci, S. Tani, and K. Miyoshi, *J. Syst. Design Dynam.* **4**, 899 (2010).
17. C.V. Suci and K. Yaguchi, *Exper. Mech. Int. J.* **49**, 383 (2009).
18. F.B. Surani, X. Kong, D.B. Panchal, and Y. Qiao, *Appl. Phys. Lett.* **87**, 163111 (2005).
19. V.A. Eroshenko, Patent USSR 1380357 A2, F 03 G, Bull. Izobr. N 3 (1996).
20. A. Laouir, L. Luo, D. Tondeur, T. Cachot, and P. Le Goff, *Am. Inst. Chem. Eng.* **49**, 764 (2003).
21. V.A. Eroshenko and Ya.G. Grosu, *Promyshl. Teplotekhn.* **33**, 73 (2011).
22. E.W. Washburn, *Phys. Rev.* **17**, 273 (1921).
23. L. Guillemot, *Ph.D. thesis* (Institut National des Sciences Appliquees de Lyon, 2010).
24. V.A. Eroshenko and S.G. Tkachenko, *Ukr. Fiz. Zh.* **38**, 1789 (1993).
25. V.S. Egorov, A.G. Portyanoi, A.P. Sorokin, V.G. Maltsev, and R.M. Voznesenskii, Patent Russia RU (11) 2138086 (13) C1 (<http://www.findpatent.ru/patent/213/2138086.html>).

26. S.L. Randzio, Chem. Soc. Rev. **25**, 383 (1996).
27. S.L. Randzio and J.-P.E. Grolier, Anal. Chem. **70**, 2327 (1998).
28. S.L. Randzio, Ch. Stachowiak, and J.-P.E. Grolier, J. Chem. Thermodyn. **35**, 639 (2003).
29. D.S. Nyce, *Linear Position Sensors: Theory and Application* (Wiley-Interscience, Hoboken, NJ, 2004).
30. B.K. Greve, K.L. Martin, P.L. Lee, P.J. Chupas, K.W. Chapman, and A.P. Wilkinson, J. Am. Chem. Soc. **132**, 15496 (2010).
31. A. Rebello, J.J. Neumeier, Z. Gao, Y. Qi, and Y. Ma, Phys. Rev. B **86**, 104303 (2012).
32. C.W. Li, T. Xiaoli, J.A. Munoz, J.B. Keith, S.J. Tracy, D.L. Abernathy, and B. Fultz, Phys. Rev. Lett. **107**, 195504 (2011).
33. J.P. Attfield, Nature **480**, 465 (2011).
34. O.V. Ievtushenko, V.A. Eroshenko, Y.G. Grosu, J.-M. Nedelec, and J.-P. E. Grolier, Phys. Chem. Chem. Phys. **15**, 4451 (2013).
35. N.L. Johnson, S. Kotz, and N. Balakrishnan, *Continuous Univariate Distributions, Vol. 1* (Wiley, New York, 1994).
36. T.G. Plachenov and S.D. Kolosentsev, *Porosimetry* (Khimiya, Leningrad, 1988) (in Russian).
37. V.A. Eroshenko and A.Yu. Fadeev, Ross. Khim. Zh. **40**, 92 (1996).
38. L. Coiffard, and V. Eroshenko, J. Colloid Interface Sci. **300**, 92 (2006).
39. *NIST Chemistry Web Book* <http://webbook.nist.gov/chemistry/>.
40. R.C. Tolman, J. Chem. Phys. **17**, 333 (1949).

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ЯВИЩЕ АНОМАЛЬНОГО ВІД'ЄМНОГО ТЕРМІЧНОГО РОЗШИРЕННЯ У КОНДЕНСОВАНІЙ ГЕТЕРОГЕННІЙ ЛІОФОВНІЙ СИСТЕМІ

Резюме

У роботі експериментально підтверджено явище зменшення об'єму гетерогенної ліофобної системи (ГЛС) при збільшенні її температури, так зване явище від'ємного термічного розширення (ВТР). Показано, що для дослідженої ГЛС "сілікаліт-1 + вода" величина ВТР більш ніж на порядок перевищує показники ВТР для відомих матеріалів. Пояснено фізичні принципи, що лежать в основі отриманого явища та запропоновано математичну модель для його опису.