EXPERIMENTAL ARTICLES

UDC 544.7+543.429.23+615.322 https://doi.org/10.15407/biotech11.06.029

INFLUENCE OF ENVIRONMENT AND HYDROPHOBIC SILICA ON WATER BINDING IN COMPOSITES CONTAINING MILLED MEDICAL PLANTS

V. V. Turov[1]
T. V. Krupska[1]
A. P. Golovan[1]
L. S. Andriyko[1]
G. V. Ostrovska[2]
O. O. Kalmykova[2]
P. Jovaisas[3]
R. Bieliauskiene[3]
M. T. Kartel[1]

[1]Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine, Kyiv

[2]ESC "Institute of Biology" of Taras Shevchenko National University of Kyiv, Ukraine

[3]"*Silicio Biotechnologijos*" Company, Vilnius, Lithuania

E-mail: krupska@ukr.net

Received 30.10.2018
Revised 07.11.2018
Accepted 28,12.2018

The aim of the work was to study the effect of methylsilica additions and deuterochloroform hydrophobic medium on the water state in a phytocomposite system "Lymphosilica".

The water state in a Lymphosilica composite material, created by mechanochemical activation of a mixture of milled medicinal plants and wetting-drying silica A-300 was studied by low-temperature ^{1}H NMR spectroscopy. The parameters of bound water layers in the initial composite and hydrated mixtures with methylsilica in air and hydrophobic media were measured. It was shown that liquid and solid hydrophobic agents reduced the binding of water with the cellulose components of medicinal plants. This can be used to control desorption rate of the bioactive complex for oral and transdermal use such herbal biological active components.

Key words: nanocomposite, hydrophobic silica.

Recent years saw a trend to minimize the potential load on the body during medical treatment, which led to wide application of biotechnologically produced bioactive compounds extracted from medical plants or synthesized by microorganisms [1–3]. There also are tisanes or dry herbal blends taken orally individually or in combination, for example, with highly dispersed silica [4, 5]. Several kinds of preparations (food supplements) are prepared in Ukraine, sold under the common name of Phytosils, to treat different kinds of diseases [6]. The filling substance (highly dispersed silica) fulfills several functions at once: detoxification, due to absorption of the mineral component of protein-derived toxins; regulation of the rate of release of the bioactive complex from the plant component due to nanosilica's strong effect on the ability of cellulose micro fibrils to hold water; and therefore, desorption of bioactive substances [7–9], as well as formation of the gastrointestinal mucous layer between the silica particles and the components. The layer consists of weakly structured water forms which increase the bioaccessibility of poorly soluble substances [10, 11].

A promising direction of functionalization for composites containing plant materials can be the construction of complex systems which contain hydrophilic silica and its methylated analogue, methylsilica. The latter

is produced by grafting a thin hydrophobic layer by substituting silanol groups with methyl ones [12, 13]. Such composite systems can be used both orally and as part of either medical or cosmetic transdermal devices. In this case, the parameter limiting the rate and degree of the bioactive complex release can be the water binding energy — the lower it is, the easier it is for the composite releases the substances. The low temperature ^{1}H NMR-spectroscopy is an efficient method to measure parameters of water bound by highly disperse and porous materials [14–17]. The change in Gibbs free energy (ΔG) and the radius (R) of adsorbed water clusters are functions of the depression of the its freezing temperature (T –273 K), and the structure of hydrogen bond nets *vs* chemical shift (δH).

Thus, the aim of this work was to study the effect of methylsilica (MS) additions and hydrophobic medium ($CDCl_3$) on the water state in a phytocomposite system "Lymphosilica", a dietary supplement prepared in the Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine (TU U 10.8-03291669-005:2017) as a supplement for lymph and blood purification.

Materials and Methods

Hydrophilic (A-300) and hydrophobic (AM1-300) silica were synthesized by Research experimental plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine. The phytocomposite system Lymphosilica includes wetting-drying highly disperse silica A-300 (Hydrosil, TU U 20.1-3291669-015:2016) and milled medicinal plants (*Hibiscus sabdariffa* flowers, *Calendula officinalis* flowers, *Echinacea purpurea* flowers, leaves of *Taraxacum officinale*, *Calluna vulgaris* and roots of *Elytrigia repens*). Silica A-300 was wetting-dried to bulk density ρ_d = 300 mg/cm^3 (dry) after the technique described in [18, 19]. After addition to dry composite 1000 mg/g distilled water, its bulk density increased to ρ_d = 470 mg/cm^3. To prepare a composite system with a hydrophobic component (AM1 with bulk density ρ_d = 50 mg/cm^3), an equal or half mass of nanosilica AM1 was added to dry Lymphosilica, after which the mixture was carefully blended in a ceramic mortar and then distilled water was added in an amount of 1000 mg/g of dry mixture. Wetted powder was subjected to high mechanical load (intense masticating with a ceramic pestle) until a homogeneous compact mass was obtained of density ρ_d = 760 mg/cm^3. Similar procedure was followed to transfer the hydrophobic silica AM1 or initial silica into aqueous medium.

Methylsilica was transferred to aqueous medium by mechanically masticating equal masses of AM1 and water under high pressure for 20–30 min. After 10–15 min the powder density increased, and 20–30 min later it (and the water) formed a thick compact layer on the mortar's sides that was cleared off with a stainless steel spatula. The initial density of the compacted AM1/water composite was about 1000 mg/cm^3, yet when the substance was lightly ground and placed into a 5 mm NMR ampoule it decreased somewhat to 700 mg/cm^3. Thus, we compared the characteristics of water between particles in hydrophobic and hydrophilic kinds of silica, having bulk densities ρ_d = 700 and 600 mg/cm^3, and water content h = 1125 mg/g and 1 000 mg/g, respectively.

The ^{1}H NMR spectra were recorded using a Varian 400 Mercury spectrometer of high resolution with an operating frequency of 400 MHz. Eight probing 60° impulses of 1 μs duration were used with a bandwidth of 20 kHz. The temperature was controlled by means of a Bruker VT-1000 device with an accuracy of ± 1 deg. The measurements were taken in 5 mm measuring ampoules. As hydrophobic dispersion medium deuterated chloroform with 99.9% Deuterium was used. To determine water binding in the composites temperature dependencies of signal intensity in unfreezing water during sample heating from 200–210 K to 280–285 K were measured. Signal intensity was determined by integrating spectra with null line correction. Relative mean errors were less than %10± for ^{1}H NMR signal intensity for overlapped signals, and ±5% for single signals. Since the amount of water in samples was 1 000 mg/g, signal intensities were used to calculate the dependence of unfreezing water concentration (C_{uw}) on temperature, and then employing the empiric ratio obtained by calculation of Gibbs free energy for ice [20].

$$\Delta G_{ice} = -0.036(273.15 - T), \qquad (1)$$

where $\Delta G(C_{uw})$ was calculated. Integrating it over the whole range of change for C_{uw} interfacial water energy was computed which determines the summary decrease in free energy of water due to the presence of interfaces [14–17].

$$\gamma_S = -K \int_0^{C_{uw}^{max}} \Delta G(C_{uw}) dC_{uw}, \qquad (2)$$

where C_{uw}^{max} is the amount of unfreezing water at T = 273 K.

Size distribution for clusters of adsorbed water was calculated according to Gibbs-Thomson equation:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl} T_{m,\infty}}{\Delta H_f \rho R}, \qquad (3)$$

where $T_m(R)$ is melting temperature of ice in the pores (voids) of radius R, $T_{m,\infty}$ — melting temperature of bulk ice, ρ — density of the solid phase, σ_{sl} — the energy of the solid-liquid interaction (for example, via hydrogen bonds), ΔH_f — the bulk enthalpy of melting. For practical use, equation (1) can be applied as $\Delta T_m = (k/R)$, where the k constant, for many heterogeneous systems containing water is close to 50 degree·nm [21].

TEM microphotography was taken at room temperature by transmission microscope Hitachi-600 (Hitachi, Ltd, Tokyo, Japan).

Microphotography of powders and emulsions was taken using microscope Primo Star (Zeiss, Germany) in reflected and transmitted light at ×100 and ×400.

Statistic analysis. The accuracy of measuring the thermodynamic parameters of interfacial water from NMR spectroscopy data was determined by the accuracy of measuring the sample temperature (± 0.5 degrees) and the intensity of the NMR signals. The signal intensity was measured by integrating them on the assumption of a Gaussian line shape and phase correction of the zero line for each spectrum. Such a procedure made it possible to ensure accuracy of integration not less than 10%. The accuracy of determining the chemical shift was no worse than ± 2%, and the magnitude of interfacial energy was no worse than 15%.

Statistical analysis for a series of samples studied was not carried out, since the repetition of measurements did not lead to changes in the temperature dependences of changes in the intensity of the NMR signal. In physicochemical experiments, in contrast to biological experiments, there is no separate control experience. We monitor changes in physicochemical parameters, such as temperature, chemical shift, signal intensity, etc. Therefore, statistical processing differs from that when a series of similar experiments is carried out and the variation of results due to individual differences in biological objects is observed. The total error of our experiments is determined by the errors in the measurement accuracy of parameters such as temperature, signal intensity, etc. When repeating experiments, a complete reproduction of such dependences as C (T) or δ (T) is usually observed.

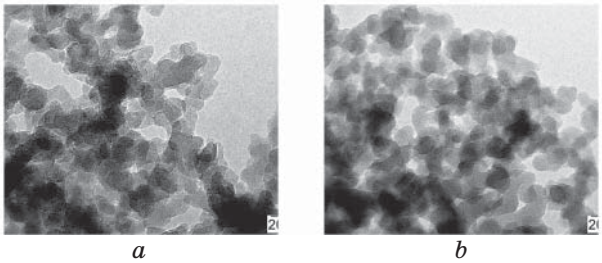
Results and Discussion

The TEM images of samples with different component ratios (70% A-300 + 30% AM1 and 80% AM1+20% A-300) are rather similar for composites made by mixing followed by intense mastication in a ceramic mortar of mixtures of hydrophobic and hydrophylic silicas (Fig. 1). There are clearly visible primary silica particles which due to inter-particle interactions form preparations having secondary nanoscaled pores. Primary particles for both kinds of silica are about 10 nm. TEM images confirm that chemical modification of nanosilica causes almost no changes in size and shape of primary particles.

To characterize specific features of composite systems with nanosilicas and milled medical plants, Fig. 2 shows microphotos of composites made with some of the plants used in Lymphosilica which have natural coloring — *Hibiscus sabdariffa* flowers (red, Fig. 2, *a*, *b*) and *Calendula officinalis* (yellow) (Fig. 2, *c*, *g*).

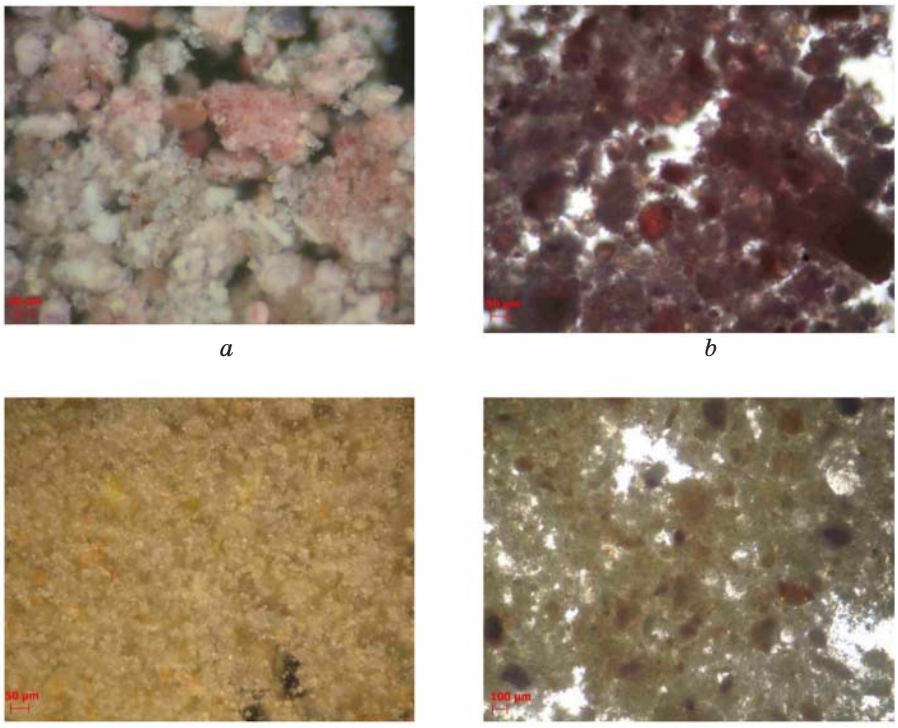
Mechanic activation leads to homogeneous composite systems in which plant particles and silica aggregates make up a compact substance and are in close contact with one another. For a composite obtained by intense mastication of Lymphosilica with equal mass of methylsilica (AM1) and 1 000 mg/g H_2O, there were also homogeneous composite systems colored mostly by *Hibiscus sabdariffa* flowers (Fig. 3).

Low temperature ^{1}H NMR-spectroscopy was used to study composite systems with water for Lymphosilica and its mixtures with methylsilica AM1/1 ,1 and 1/2. Fig. 4 shows the spectra of water in the Lymphosilica/H_2O (CH_2O = 1000 mg/g) composite recorded at different temperatures in air and in weakly



a *b*

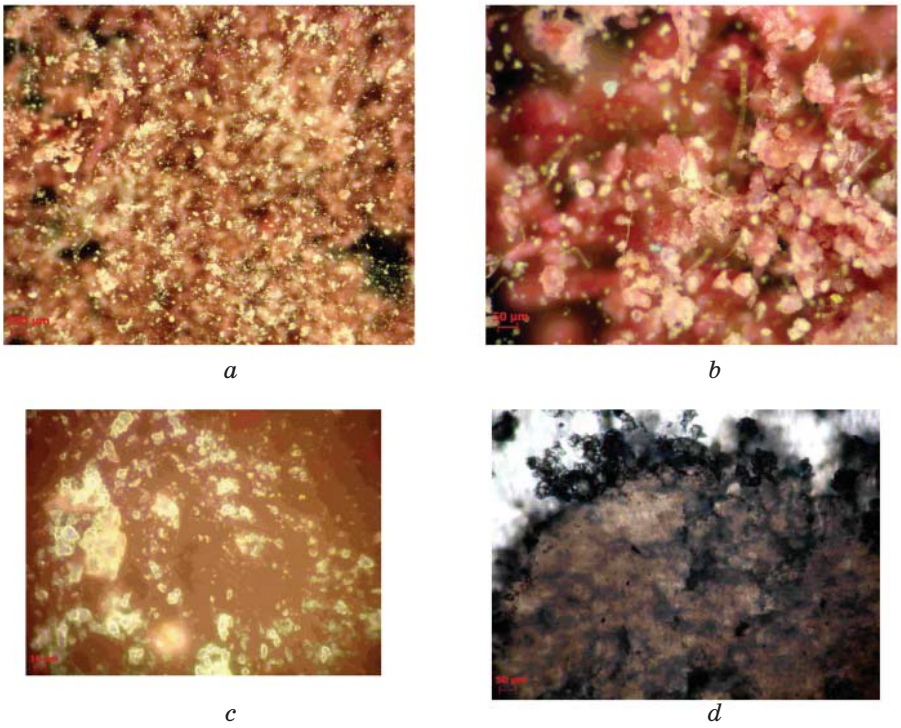
Fig. 1. **TEM images of mixtures of hydrophobic and hydrophylic nanosilicas:**
a — 70% A-300 + 30% AM1;
b — 80% AM1+20% A-300
Here and after: results of typical experiment are presented



a *b*

c *d*

Fig. 2. **Microphotographs of composites based on hydrocompacted silica and *Hibiscus sabdariffa* flowers (*a*, *b*) or *Calendula officinalis* (*c*, *d*), taken in** reflected (*a*, *c*) and transmitted (*b*, *d*) light



a *b*

c *d*

Fig. 3. **Microphotographs of composite system 1/1, obtained by mechanic activation mixture of the Lymphosilica with AM1:** in reflected (*a*–*c*) and transmitted (*d*) light

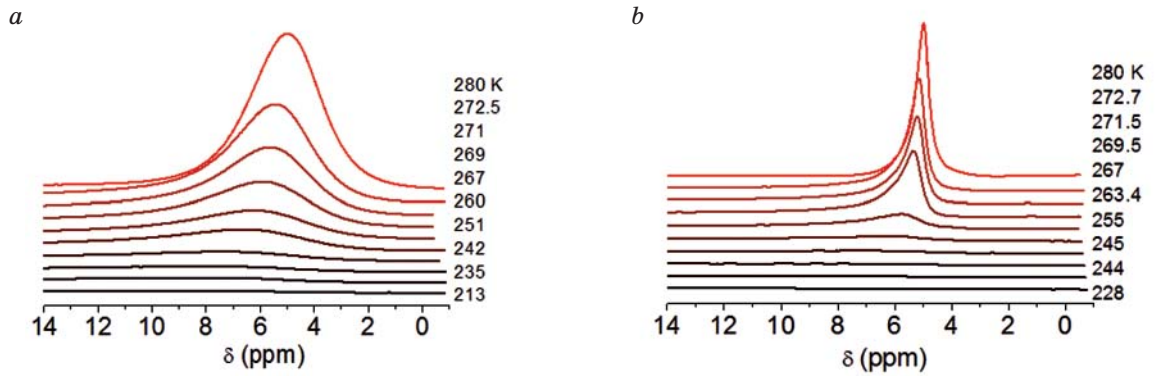


Fig. 4. **^{1}H NMR spectra of water in the composite system Lymphosilica/H_2O in:** air (*a*) and in $CDCl_3$ (*b*) recorded at different temperatures

polar organic solvent, deuterated chlorophorm, which is a good model for hydrophobic salves used in cosmetics. For composites including methylsilica A1 the spectra are similar to Fig. 4 and thus are omitted.

^{1}H NMR spectra of samples that were precooled to T = 200–210 K, demonstrate only one adsorbed water signal with intensity decreasing with temperature due to partial freezing of bound water. The stronger water-surface interactions or the narrower the clusters including interfacial water, the lower the temperature of freezing [15]. Chemical water shift changes from δH = 5 ppm at T = 285 K to δH = 7–9 ppm at T = 200–220 K. According to the classification [14–17] all adsorbed water can be classified as strongly associated, with each molecule forming two to three hydrogen bonds.

Temperature dependences of the content of unfrozen water and chemical shift are presented in Fig. 5. The dependences are antisymbatic: lower unfrozen water concentration is accompanied by larger chemical shift. This may be due to two main factors: an increase in the orderliness of water associates with a decrease in temperature and an increase in the contribution from water interacting with the proactive (electron donor) centers of the bioactive complex that is part of medicinal plants. In particular, Lymphosilica can be expected to contain a lot of organic acids (*Hibiscus*) with which the water molecules can form strong hydrogen bonds that increase chemical shift of adsorbed water. This is a possible reason for the observed values of chemical shift which are significantly larger than those of tetragonal coordination of water in hexagonal ice [22].

Another specific feature of temperature dependences of chemical shift of adsorbed water is the presence of inflection points at temperatures around T = 240 K and T = 270 K. These inflections might be caused to temperature intervals where the probability of formation of water poly-associates with different water association degrees' changes. Considering that the chemical shift of tetrahedrally coordinated water (hexagonal ice) is δH = 7 ppm [22], on the curves of δH(T) this value corresponds to an inflection in the range of T = 240–250 K. Probably, at lower temperatures the contribution of water bound to acid molecules increases. The inflection of dependences δH(T) near the melting point of bulk ice is caused by the increase in amount of unfrozen water and therefore with its structure nearing structure of liquid water with its typical partially destroyed net of hydrogen bonds [23–25].

The dependences of changes in Gibbs free energy *vs* the content of unfrozen water can be (Fig. 6) estimated from integral intensity of the ^{1}H NMR spectra recorded at different temperatures, according to formula (1). Thermodynamic parameters of layers of bound water — the amount of strongly and weakly bound water (C^S_{uw} and C^W_{uw}, respectively), the maximum reduction of free energy in the strongly bound layer (ΔGS), and the value of interfacial energy (γS) of Lymphosilica-based composite systems are shown in Table 1. In this case, weakly bound water is that part of unfrozen water which freezes at T > 265 K ($\Delta G < -0.5$ kJ/mol).

Lymphosilica- and nanosilica-based composite systems are multi-component. That complicates analyzing changes in their properties depending on composition. Therefore, we studied the parameters of interaction with water of the initial silicas (wetting-drying A-300 and AM1) at close hydration degrees. The silica A-300 has

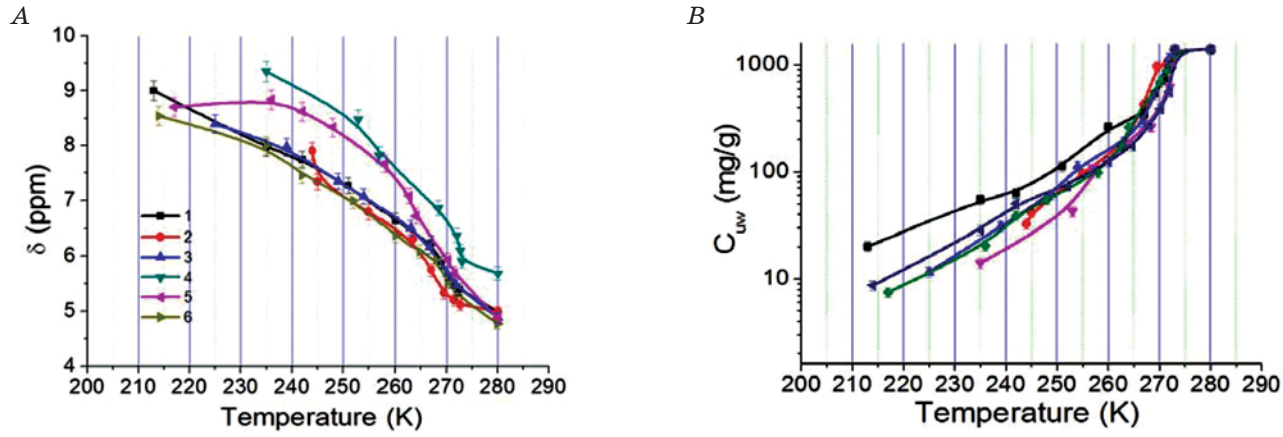


Fig. 5. **Temperature dependences of the content of unfrozen water (*B*, C_{uw}) estimated from integral intensity of the ^{1}H NMR spectra recorded at different temperatures, and its chemical shift (δ, ppm, *A*) for Lymphosilica-based composites:**
1 — Lymphosilica in air; *2* — Lymphosilica in $CDCl_3$; *3* — 1Lymphosylica/1AM1 in air; *4* — 1Lymphosilica/1AM1 in $CDCl_3$; *5* — 2Lymphosilica/1AM1 in air; 6 — 2Lymphosilica/1AM1 in $CDCl_3$

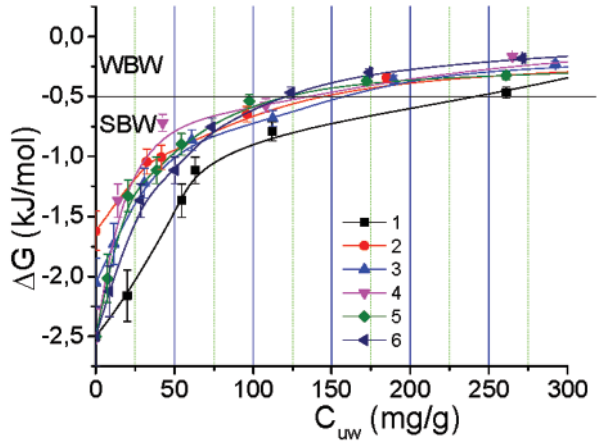


Fig. 6. **Dependences of change in Gibbs free energy on concentration of unfreezing water in Lymphosilica-based composite systems, where:**
1 — Lymphosilica in air; *2* — Lymphosilica in $CDCl_3$; *3* — 1Lymphosylica/1AM1 in air; *4* — 1Lymphosilica/1AM1 in $CDCl_3$; *5* — 2Lymphosilica/1AM1 in air; *6* — 2Lymphosilica/1AM1 in $CDCl_3$

hydrophilic surface due to the presence of a large number of hydroxyl groups [12], and so it can absorb a lot of water that clusters at the surface, and the cluster size depends on the morphology of interparticle space and hydration degree [15]. Water absorption by A-300 is thermodynamically favorable, since the process is exothermic. On the surface of hydrophobic silica AM1 there are practically no centers of primary adsorption of water. So, transferring it into aqueous medium requires certain energy expenditure — the wetting process is endothermic. Such effect can be obtained by mechanical and chemical means, after the prolonged mastication of silica with water. As a result of mechanical loading, air is removed from the interparticle gaps of hydrophobic silica and is replaced by water, which interacts with the surface only by the mechanism of hydrophobic hydration [26–28].

Dependences of the changes in concentrations of unfreezing water on temperature (calculated on their basis dependencies of changes in Gibbs free energy on the concentration of unfreezing water for the hydrophilic (A-300) and hydrophobic (AM1) silicas) are presented on Fig. 7, and the characteristics of the layers of bound water in air and in CDCl3 are given in Table.

According to the data in Table, the interfacial energy values are determined by two parameters, the concentration of strongly bound water and the maximum reduction in free energy in the layer of strongly bound water (Δ*GS*). The last parameter determines the change in free energy in that part of water which freezes at the lowest temperature. This may be that part of the interfacial water, which borders on the surface and is associated with the primary adsorption centers, or water that forms the smallest clusters, and, which according to the Gibbs-Thomson equation (eq. 3) freezes at the lowest temperatures. To clearly show the influence of the composite content on the water binding in conditions of comparable hydration of the surfaces, a diagram of changes in γS and radius distribution of adsorbed water clusters is shown in Fig. 8.

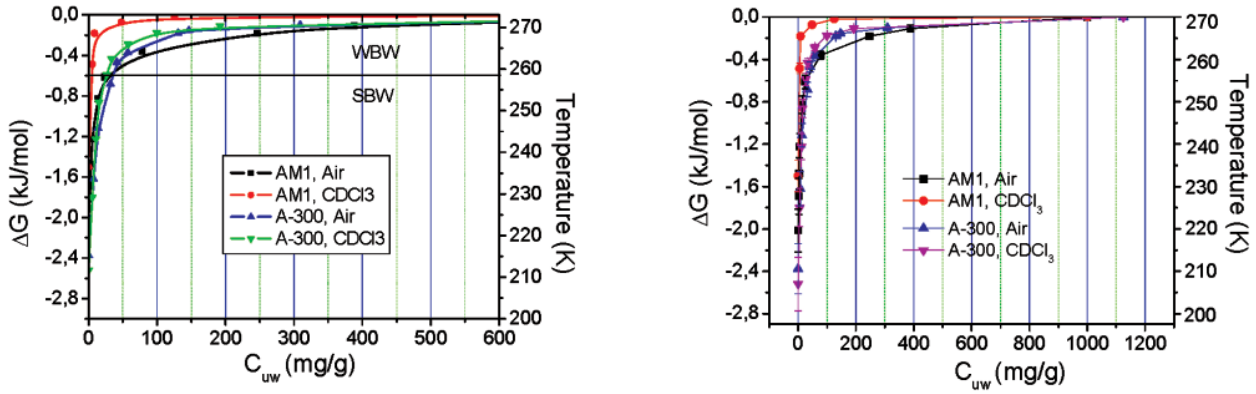


Fig. 7. **Temperature dependences of the content of unfrozen water (C_{uw}) estimated from integral intensity of the ^{1}H NMR spectra recorded at different temperatures, and changes in the Gibbs free energy ΔG vs. C_{uw} (for A-300 and AM1 samples with constant hydration upon NMR measurements:** h = 1.1 (g/g) in air and in $CDCl_3$

Characteristics of water bound to Lymphosilica-based composite systems in various media

Sample	Medium	C^S_{uw} (mg/g)	C^W_{uw} (mg/g)	ΔGS (kJ/mol)	γS, (J/g)
Lymphosilica/H_2O	Air	250	750	−2.75	19,9 ± 15%
	$CDCl_3$	150	850	−1.7	17.5 ± 15%
1 Lymphosilica/1AM1/H_2O	Air	160	840	−2.0	16,4 ± 15%
	$CDCl_3$	140	860	−2.5	11.4 ± 15%
2 Lymphosilica/1AM1/H_2O	Air	130	870	−2.5	16,3 ± 15%
	$CDCl_3$	115	875	−2.5	12.2 ± 5%
A–300 /H_2O	Air	50	950	−2	11.7 ± 15%
	$CDCl_3$	10	990	−1.5	4.8 ± 15%
AM1 /H_2O	Air	40	1085	−2.4	2.5 ± 15%
	$CDCl_3$	30	1095	−2.5	3.2 ± 15%

Interfacial energy of water bound with hydrophobic or hydrophilic silicas (Table) turned out to be significantly lower than with Lymphosilica, and this was true for both air and for chlorophorm media. Therefore, binding is mostly caused by the plant component.

Maximum values of γS = 19.9 J/g were recorded for Lymphosilica in air. In $CDCl_3$ it decreases to 17.5 J/g. Addition of hydrophobic silica results in decreasing of the interfacial energy by 3-4 J/g (Fig. 8, Table). The effect is even stronger in chlorophorm, where the decrease in γS reaches 7 J/g. Comparing values of interfacial energy with size distribution of adsorbed water cluster it can be concluded that in chloroform, or if the composite contains solid hydrophobic component, the probability of relatively smaller water clusters increases. So, if for the Lymphosilica in an air medium a significant part of water is in clusters with a radius of R = 20–100 nm, then for the same sample in a liquid hydrophobic medium the maximum value on the distribution ΔC(R) is R = 9 nm (Fig. 8, *a*). Addition of the solid hydrophobic component (hydrated AM1) to the composite lead to the similar results. There is also one maximum in the distribution of $\Delta C(R)$, and practically no clusters of $R > 50$ nm. Liquid hydrophobic medium increases the contribution of small clusters of adsorbed water. Consequently, using solid and liquid hydrophobic additives it is possible to regulate the energy of water binding in composite systems based on medicinal plants and mineral adsorbents over a wide range.

The mechanism of influence of hydrophobic agents on the binding of water in milled medicinal plants may be different. Thus, for highly disperse materials it has been shown that the medium of liquid weakly polar substances reduces the interaction of water with the surface due to liquid penetration into the gaps between the clusters of adsorbed water and the surface which reduces the possibility

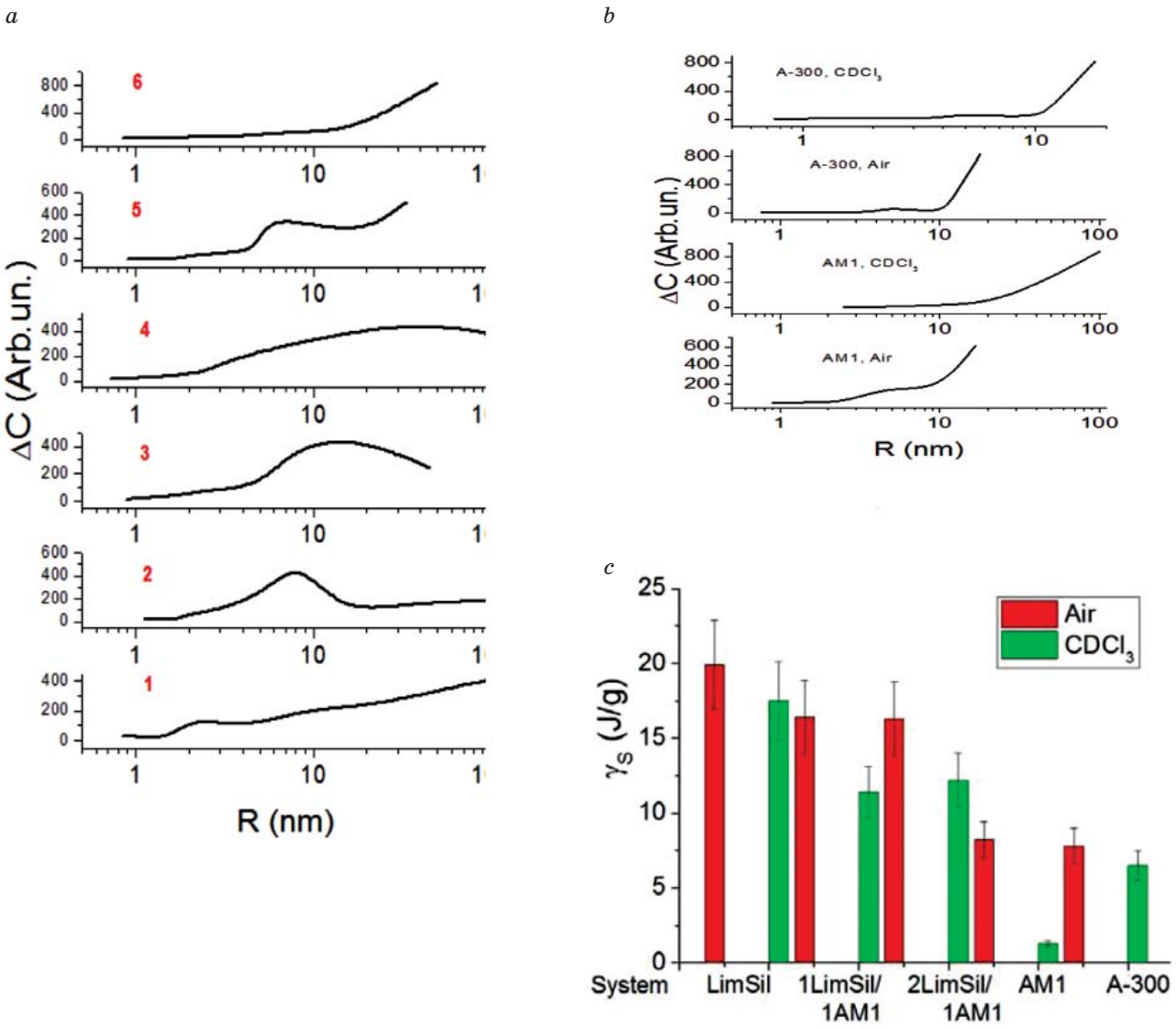


Fig. 8. **Size distributions of adsorbed water cluster sizes for Lymphosilica-based composites:** (*a*) (where: *1* — Lymphosilica in air; *2* — Lymphosilica in $CDCl_3$; *3* — 1Lymphosylica/1AM1 in air; *4* — 1Lymphosilica/1AM1 in $CDCl_3$; *5* — 2Lymphosilica/1AM1 in air; 6 — 2Lymphosilica/1AM1 in $CDCl_3$) and the initial hydrophilic and hydrophobic silicas (*b*), and the diagram of changes in interface water energy depending on the composite content (*c*)

of water clusters to interact with the primary centers of water adsorption [17]. For a multi-component system such as dietary supplement Lymphosilica this kind of hydrophobic liquid effect can be expected for the highly dispersed oxides. The influence on the plant component might be more complex since water binding in the space between cellulose fibers [29] depends on interaction with hydrophilic silica [8].

A method of creating dense, hydrated composite systems based on milled medicinal plants and a mixture of hydrophobic and hydrophilic silica was developed It is shown that for dietary supplement "Lymphosilica" created on the basis of milled medicinal plants and hydrophilic silica, the amount of water binding is several times higher than its binding energy with both hydrophilic and hydrophobic silica. Probably this due to the retention of a significant part of water in space, formed by cellulose fibrils.Using additives of hydrophobic silica or liquid hydrophobic medium, makes it possible to control free energy of water binding. These results can be used to create oral and transdermal medicinal preparations.

The work contains the results of research conducted with the grant support of the State Fund for Fundamental Research on the competition project F76/21.

REFERENCES

1. *Georgievskiy V. P., Komissarenko N. F., Dmytruk S.* E. Biological activity substances of medical plants. *Novosibirsk: Nauka*. 1990, 332 p. (In Russian).
2. *Fumagalli C.* Succinic acid and succinic anhydride. In Kirk-Othmer Encyclopedia of Chemical Technology,4th ed.; Kroschwitz J. I., Howe-Grant M., eds. *Wiley: New York, NY, USA*. 1997, V. 22, P. 1074–1102.
3. *Turyshev S. N.* Modern phytotherapy. *Moskva: GEOTAZ-Medicine*. 2007, 448 p. (In Russian).
4. *Turov V. V., Krupska T. V., Golovan A. P., Andriyko L. S., Kartel M.* T. Composite systems of prolonged action on the basis of milled medicinal plants and nanosilicas. *Science and Innovation*. 2017, 13 (2), 59–67. (In Ukrainian). https://doi.org/10.15407/scin13.02.059
5. *Turov V. V., Krupskaya T. V., Golovan A. P., Kartel N. T.* Composite systems based on milled flowers *Calendula officinalis* and nanosilica A-300. *Reports of the National Academy of Sciences of Ukraine*. 2017, N 4, P. 76 — 83. (In Russian).
6. *Chuiko A. A., Pogorelyy V. K., Barvinchenko V. N., Lipkovskaya N. A., Kovtyukhova N. I., Turov V. V.* Physical-chemical and clinical justification of the effectiveness of phytosyl family drugs. *Chemistry, Physics and Technology of Surface*. 1999, V. 3, P. 3–9. (In Russian).
7. Structure and physico-chemical properties of celluloses and nanocomposites based on them. Ed. *Alyoshyna L. A., Gurtova V. A., Melech N. V. Petrozavodsk: Publishing house of PetrSU*. 2014, 240 p. (In Russian).
8. *Shulga O. V., Kerchhoff J., Turov V. V.* The Influence of the Dispersed Oxides on the Interface Energy of the Microcristalline Cellulose in Water Suspension. Methoporous and Microporous Materials. *Chemistry, Physics and Technology of Surface*. 2001, N 4–6, P. 267–274.
9. Medical chemistry and clinical application of silica dioxide, Ed. *Chuiko A. A. Kyiv: Nauk. dumka*. 2003, 416 p. (In Russian).
10. *Turov V. V., Morozova L. P., Shtatko O. I., Lutsyuk M. B., Turov A. A., Taran I. V.* Influence of contact with nanosilica A-300 on the hydration of the subcellular material of the rat's small intestine. *Chemistry, Physics and Technology of Surface*. 2013, 4 (1), 67–77. (In Ukrainian).
11. *Krupska T. V., Turova A. A., Gun'ko V. M., Turov V. V.* Influence of highly dispersed ma terials on physiological activity of yeast cells. *Biopolymers and Cell*. 2009, 25 (4), 290–297.
12. *Tertykh V. A., Belyakova L. A.* Chemical reactions involving the surface of silica. *Kyiv: Nauk. dumka*. 1991, 246 p. (In Russian).
13. *Protsak I. S., Tertykh V. A., Bolbukh Yu. M., Sternik D., Derylo-Marczewska A.* Synthesis and properties of fumed silicas modified with mixtures of poly(methylphenylsiloxane) and dimethyl carbonate. *World J. NanoSci Engineer. (WJNSE)*. 2016, 5 (4), 152–160.
14. *Gun'ko V. M., Turov V. V., Gorbik P. P.* Water at the interface. *Kyiv: Nauk. dumka*. 2009, 694 p. (In Russian).
15. *Gun'ko V. M., Turov V. V.* Nuclear Magnetic Resonance Studies of Interfacial Phenomena. *New York: Taylor & Francis*. 2013, 1006 p.
16. *Gun'ko V. M., Turov V. V., Bogatyrev V. M., Zarko V. I., Leboda R., Goncharuk E. V., Novza A. A., Turov A. V., Chuiko A. A.* Unusual properties of water at hydrophilic/hydrophobic Interfaces. *Adv. Colloid. Interf. Sci*. 2005, 118 (1–3), 125–172.
17. *Turov V. V., Gun'ko V. M.* Clustered water and ways to use it. *Kyiv: Nauk. dumka*. 2011, 316 p. (In Russian).
18. *Krupskaya T. V., Turov V. V., Barvinchenko V. M., Filatova K. O., Suvorova L. A., Kartel M. T.* Methods of sealing nano-silica. *Ukraine. Patent №105151*, March 10, 2016. (In Ukrainian).
19. *Krupskaya T. V., Turov V. V., Barvinchenko V. M., Filatova K. O., Jan-Luca I., Kartel M. T.* Influence of the "wetting-drying" compaction on the adsorptive characteristics of nanosilica A-300. *Ads. Sci. & Technol*. 2017, 36 (1–2), 300–310.
20. Thermodynamic properties of individual substances. Ed. *Glushkov V. P. Moskva: Science*. 1978, 495p. (In Russian).
21. *Petrov O. V., Furo I.* NMR cryoporometry: Principles, application and potential. *Progr. NMR*. 2009, V. 54, P. 97–122.
22. *Kinney D. R., Chaung I-S., Maciel G. E.* Water and the Silica Surface As Studied by Variable Temperature High Resolution 1H NMR. *J. Am. ChemSoc*. 1993, N 115, P. 6786–6794.
23. *Wiggins P. M., MacClement B. A. E.* Two states of water found in hydrophobic clefts: their possible contribution to mechanisms of cation pumps and other enzymes. *Internat. Rev. Cytol*. 1987, V. 108, P. 249–303.
24. *Dore J.* Structural studies of water in cinfined geometry by neutron difraction. *Chem. Phys*. 2000, V. 258, P. 327–347.
25. *Chaplin M. F.* A proposal for structuring of water. *Biophys. Chem*. 1999, V. 83, P. 211–221.
26. *Yaminsky V. V., Vogler E. A.* Hydrophobic hydration. *Curr. Opin. Colloid Interface Science*. 2001, N 6, P. 342–349.
27. *Chandler D.* Interfaces and the driving force of hydrophobic assembly. *Nature*. 2005, V. 437, P. 640–647.
28. *Mitra R. K., Verma P. K., Pal S. K.* Exploration of the Dynamical Evolution and the Associated Energetics of Water Nanoclusters Formed in a Hydrophobic Solvent. *J. Phys. Chem. B*. 2009, V. 113, P. 4744–4750.
29. *Hatakeyama T., Nakamura K., Hatakeyama H.* Determination of Bound Water Content in Polymers by DTA, DSC and TG. *Termochemica Acta*. 1988, V. 123, P. 153–161.

ВПЛИВ СЕРЕДОВИЩА ТА ГІДРОФОБНОГО КРЕМНЕЗЕМУ НА ЗВ'ЯЗУВАННЯ ВОДИ В КОМПОЗИТАХ, ЯКІ МІСТЯТЬ ПОДРІБНЕНІ ЛІКАРСЬКІ РОСЛИНИ

В. В. Туров[1]
Т. В. Крупська[1]
А. П. Головань[1]
Л. С. Андрійко[1]
Г. В. Островська[2]
О. О. Калмикова[2]
П. Йоваісас[3]
Р. Біеляускєне[3]
М. Т. Картель[1]

[1]Інститут хімії поверхні імені О. О. Чуйка НАН України, Київ
[2]ННЦ «Інститут біології» Київського національного університету імені Тараса Шевченка
[3]Підприємство «*Silicio Biotechnologijos*», Вільнюс, Литва

E-mail: krupska@ukr.net

Метою роботи було вивчити вплив додавання метилкремнезему та гідрофобного середовища дейтерохлороформу на стан води в фітокомпозитній системі дієтичної добавки «Лімфосиліка». Методом низькотемпературної ^{1}H ЯМР-спектроскопії вивчено стан води в композитному матеріалі «Лімфосиліка», що його створено механохімічною активацією суміші подрібнених лікарських рослин та гідроущільненого кремнезему А-300. Виміряно параметри шарів зв'язаної води у вихідному композиті та в гідратованих сумішах з метилкремнеземом на повітрі та в гідрофобному середовищі. Показано, що рідкий і твердий гідрофобний агенти зменшують зв'язування води з целюлозними компонентами лікарських рослин, що може бути використано для корекції швидкості десорбції біоактивного комплексу за перорального та трансдермального застосування рослинних препаратів.

Ключові слова: нанокомпозит, гідрофобний кремнезем.

ВЛИЯНИЕ СРЕДЫ И ГИДРОФОБНОГО КРЕМНЕЗЕМА НА СВЯЗЫВАНИЕ ВОДЫ В КОМПОЗИТАХ, СОДЕРЖАЩИХ ИЗМЕЛЬЧЕННЫЕ ЛЕКАРСТВЕННЫЕ РАСТЕНИЯ

В. В. Туров[1]
Т. В. Крупская[1]
А. П. Головань[1]
Л. С. Андрийко[1]
Г. В. Островская[2]
О. А. Калмыкова[2]
П. Йоваисас[3]
Р. Биеляускене[3]
Н. Т. Картель[1]

[1]Институт химии поверхности имени А. А. Чуйко НАН Украины, Киев
[2]ННЦ «Институт биологии» Киевского национального университета имени Тараса Шевченко
[3]Предприятие «*Silicio Biotechnologijos*», Вильнюс, Литва

E-mail: krupska@ukr.net

Целью работы было изучить влияние добавления метилкремнезема и гидрофобной среды дейтерохлороформа на состояние воды в фитокомпозитной системе диетической добавки «Лимфосилика». Методом низкотемпературной ^{1}H ЯМР-спектроскопии изучено состояние воды в композитном материале «Лимфосилика», созданном механохимической активацией смеси измельченных лекарственных растений и гидроуплотненного кремнезема А-300. Измерены параметры слоев связанной воды в исходном композите и гидратированных смесях с метилкремнеземом в воздушной и гидрофобной средах. Показано, что жидкий и твердый гидрофобный агенты уменьшают связывание воды с целлюлозными компонентами лекарственных растений, что может быть использовано для коррекции скорости десорбции биоактивного комплекса при пероральном и трансдермальном применении растительных компонентов.

Ключевые слова: нанокомпозит, гидрофобный кремнезем.