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Fig. 1. Adsorption isotherms of methanol vapors on control (1), methanol (2), ethanol (3), propanol (4), isopropanol (5), butanol (6), and isobutanol silica gel (7)

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Abstract

Full Text

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THE ROLE OF THE POLARITY OF THE INTERMICELLAR LIQUID AND OF THE INTENSITY OF ITS INTERACTION WITH THE SURFACE OF SILICIC-ACID HYDROGEL PARTICLES IN THE FORMATION OF THE TEXTURE OF SILICA GELS

(Presented by Academician P. A. Rebinder, 23 XII 1963)

From the general laws of physicochemical mechanics ([1]) it follows that the strength of capillary-porous gel-like catalysts and adsorbents depends on the sizes of the elementary particles composing them and on the character of the packing of the latter in the corresponding xerogels ([2]). In the case of such lyophilic systems as hydrogels (and, in general, lyogels) of silicic acid, both the sizes of the elementary particles and the geometry of their packing in the structure are apparently predetermined by the intensity of the interaction between the intermicellar liquid (i.l.) of the lyogel and the surface of the particles of the dispersed phase wetted by it ([3],[4]).

Fig. 1. Adsorption isotherms of methanol vapors on control (1), methanol (2), ethanol (3), propanol (4), isopropanol (5), butanol (6), and isobutanol silica gel (7)

An experimental study of this question for the case of silicic-acid lyogels was necessary because, up to now, the literature has contained different, sometimes completely opposite, views on the mechanism of texture formation in silica gels.

Some authors ([5–8]) believe that the degree of shrinkage of lyogels during their drying is due mainly to the surface tension of the intermicellar liquid at the liquid–air interface, whereas others ([9–11]) suppose that the main cause of contraction of the gel skeleton consists in the direct interaction of the molecules of the intermicellar liquid with the skeleton of the lyogel.

It should be noted that in all these works ([5–11]) the degree of wetting of the surface of gel particles by the intermicellar liquid was either taken to be constant ($\cos\theta \approx +1$), or was not taken into account at all. However, liquids of different polarity ([12–15]) are adsorbed differently on the polar surface of the silica-gel pores being formed and, consequently, wet it selectively in different ways.

In order to clarify the indicated theoretical questions and at the same time to obtain a series of xerogels with successively changing textural characteristics, in the present work we chose, as intermicellar liquids, the homologous series of aliphatic alcohols, in which the polarity of the individual alcohols varies regularly ([14,15]), whereas their surface tension at the interface with air remains practically constant along the series.

Silicic-acid hydrogels, prepared by the usual method from solutions of H_2SO_4 and Na_2SiO_3, were each divided into two parts. In one, the water of the hydrogel was replaced by repeated decantation with absolute alcohols

(liquid-phase replacement of the i.m.l.) and drying of the alcogels thus obtained was carried out in desiccators over calcined $CaCl_2$; all operations were performed at room temperature in order to avoid possible complicating chemical reactions between the i.m.l. and the surface of the lyogels. In the second part, the water of the hydrogel was replaced by alcohols during drying of the gel in a desiccator over $CaCl_2$ in the vapors of the corresponding alcohols (vapor-phase replacement of the i.m.l.). For all series of alcogels, control silicaxerogels were obtained from the initial hydrogels.

For each of these two methods several series of samples were obtained, and in all cases the results were readily reproducible. The structural-sorption characteristics of the silica gels obtained were determined from methanol vapor adsorption isotherms recorded in a vacuum apparatus with McBain balances.

As is seen from Figs. 1 and 2, the nature of the porosity of silica gels obtained by liquid-phase replacement of water by alcohols changes regularly on going from one alcohol to another in the homologous series: the sorption pore volume V_S and the radius of the predominant pores r increase on going from methanol to the next members of the series. Similar results were also obtained in the case of vapor-phase replacement of the i.m.l., with the sole difference that there are some deviations in the case of butanol, apparently explained by the slower replacement of water by *n*- and isobutyl alcohols, owing to the low elasticity of their saturated vapors and their low solubility in water at room temperature.

Fig. 2. Change in the volume **(1)** and radius **(2)** of pores of silica gels upon replacement of hydrogel water by normal alcohols (n_C is the number of carbon

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atoms in the alcohol molecule)

The increase in the specific surface area S upon replacement of the hydrogel water by alcohols (Table 1) is evidently explained by the fact that the alcohols, being adsorbed on the hydroxyls of the surface of the elementary gel particles, screen them with their hydrocarbon radicals.

Table 1

Physical properties of the intermicellar liquids used and structural-sorption characteristics of silica gels

Intermicellar liquid	$\sigma_{l\text{-}g}$, erg/cm^2	$\mu_y^{(*)}$, 10^{-18} CGSE	Q^{**}, cal/g	Q^{***}, erg/cm^2	I series V_S, cm^3/g	I series r, Å	I series S, m^2/g	II series V_S, cm^3/g	II series r, Å	II series S, m^2/g
Water	72.75	–	16.1	–	0.32	12	620	0.35	14	500
Methanol	22.55	1.30	14.9	250	0.69	16	640	0.78	15	–
Ethanol	22.32	2.30	14.8	205	1.00	19	770	0.79	15	630
n-Propanol	23.70	2.92	14.1	185	1.13	21	720	0.87	17	650
Isopropanol	21.24	2.84	–	–	1.15	20	810	1.04	18	900
n-Butanol	24.57	3.51	13.0	170	1.35	22	820	1.30	21	750
Isobutanol	22.98	3.48	12.4	–	1.49	22	830	1.46	31	840

* According to data of (15). ** According to data of (16). *** According to data of (17).

As a result, aging of the alcogel skeleton is slowed in comparison with the control hydrogel, i.e., the process of condensation of OH groups with formation of interparticle bonds ≡ Si—O—Si ≡ is inhibited, which decreases the degree of aggregation of the gel particles during

while high values of S are preserved. Thus, from alcogels one obtains silica gels (xerogels) with a more finely dispersed and less rigid skeleton, which facilitates the regular increase of V_S and r of silica gels with increasing molecular weight of the alcohol-forming agent.

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Fig. 3. Relationship between the volume of sorption pores of silica gels obtained from alcogels and the heats of wetting of silica gel by the corresponding alcohols (according to data [17]): 1–CH_3OH, 2–C_2H_5OH, 3–n-C_3H_7OH, 4–n-C_4H_9OH.

Figure 3: Fig. 3. Relationship between the volume of sorption pores of silica gels obtained from alcogels and the heats of wetting of silica gel by the corresponding alcohols (according to data [17]): 1–CH_3OH, 2–C_2H_5OH, 3–n-C_3H_7OH, 4–n-C_4H_9OH.

Comparing the structural-sorption characteristics of the silica gels obtained with the physical properties of the intermolecular liquids used (Table 1), one can see that σ_{lg} in the homologous series remains approximately constant, whereas the conventional dipole moment μ_u, characterizing the polarity of the intermolecular liquid [15], increases regularly in going from methanol to the subsequent alcohols; this indicates a regular increase in intermolecular interaction (cohesion) in the alcohols. This agrees well with the equally regular decrease in this same series of the heats of wetting Q of silica gels by alcohols, measured [16] for wide-pore silica gels and for nonporous aerosil [17]. Since Q characterizes the intensity of interaction of a liquid with the surface of a solid, the regular change found in the present work in V_S of silica gels with changes in the corresponding values of Q (Fig. 3) is evidence of the decisive role of the interaction of the intermolecular liquid with the surface of the lyogels (the wetting energy of this surface) in the formation of the porous structure of xerogels. The observed regular change in the structural-sorption properties of silica gels, naturally, cannot in any way be due to the value of σ_{lg} at the liquid–gas interface, which is constant in this homologous series.

Fig. 3. Relationship between the volume of sorption pores of silica gels obtained from alcogels and the heats of wetting of silica gel by the corresponding alcohols (according to data [17]): 1–CH_3OH, 2–C_2H_5OH, 3–n-C_3H_7OH, 4–n-C_4H_9OH.

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