HEAT OF IMMERSION OF SILICA IN WATER

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ABSTRACT

The heats of immersion of thermally treated silicas and metal modified silicas, obtained from colloidal silica, were studied in water at 298 K. Silica was heat-treated in the range 383–1273 K in air. The thermal treatment effects on the water contents, specific surface areas, and the change of crystal structure were investigated and discussed. The values of the heat of immersion in water are independent of the specific surface areas of silicas in the range 125–240 m^2 g^{-1}. The results indicate that there is no maximum of the function: heat of immersion vs. thermal treatment temperature. Owing to the purity of the SiO_2 obtained, the change of the amorphous into the crystal structure (α-cristobalite) takes place at 1573–1673 K.

INTRODUCTION

Numerous investigations have been carried out in order to determine the heat of immersion (ΔH_i) of different kinds of silica (SiO_2) in both water and organic solvents. A literature survey [1] reveals considerable discrepancies and disagreements among the ΔH_i values obtained in different laboratories and, very often, obtained by the same authors. The heats of immersion of SiO_2 powders vary in a wide range: from 18 to 940 mJ m^{-2} in water and from 30 to 450 mJ m^{-2} in organic solvents. Obviously, the structure and the surface area composition of SiO_2 do not only differ from powder to powder but are modified significantly by the conditions under which the samples are prepared.

The results obtained for different SiO_2 samples, outgassed in vacuum, show that there is a maximum in the curve of the heat of immersion in water against outgassing temperature. This maximum is observed at a temperature $T = 573 \pm 50$ K [2–9]. Three hypotheses have been found in the literature explaining this phenomenon. According to the first one [2–4], the hydroxyl groups at the SiO_2 surface form hydrogen bonds with water molecules during immersion. Condensation of the surface hydroxyl groups takes place at temperatures above 573 K. Transformation of the silanol groups into silo-

xane groups, which when immersed in water cannot be easily rehydroxyl-
ated, lowers the heat of immersion. On the other hand, the surface hydroxyl
groups are at lower temperatures partially covered by a proportion of the
physically adsorbed water molecules and this contributes to the lowering of
the heat of immersion. The highest concentration of the surface hydroxyl
groups exists at a temperature of 573 ± 50 K and as a result a maximum for
the heat of immersion occurs.

According to the second hypothesis [5,8–10], the thermal treatment,
because of the condensation of the surface hydroxyl groups, leads to the
formation of a siloxane surface. Immersion of the SiO_2 samples with a
siloxane surface in water causes the formation of hydroxyl groups. The heat
of immersion rises since the dehydroxylation increases with increasing ther-
mal-treatment temperature. After a certain temperature of the thermal
treatment, the heat of immersion decreases as a consequence of the siloxane
surface formed which cannot be easily rehydroxylated.

Quite opposite to the above explanations, Tyler et al. [7] stated that the
heat of immersion of SiO_2 in water and in benzene contains a term which
reflects disturbances of the water structure layer surrounding the solid. The
fact, already well known in the literature, is that the water near the SiO_2
surface differs considerably from the water in the bulk liquid state and that
it is dependend on the sample porosity.

A recent paper by Kondo et al. [11], an attempt to investigate the heat of
immersion of silica gel in water and in some organic solvents, reveals that
there is no simple dependence of the heat of immersion on the thermal-treat-
ment temperature. These authors also indicate the absence of the maximum
discussed earlier. Instead, the values for the heats of immersion in water and
in aliphatic alcohols are proportional to the density of the surface OH
groups in the region 0–4 OH nm^{-2}.

A great number of authors [2,3,8,9,12–15] have shown that the heat of
immersion of SiO_2 in water and other polar solvents depends primarily on
the water content in a sample and it is proportional (at least qualitatively) to
the number of hydroxyl groups at the surface and their ability to interact
with the bulk water.

Experimental data obtained by some authors suggest that the heat of
immersion of SiO_2 in water can depend on the specific surface area of the
powder. Hackerman and co-workers [4,16,17] have reported that the values
of the heats of immersion of the powders with relatively large particle size
($S_p < 3$ m^2 g^{-1}) are greater by a factor of 2 or more than the values obtained
for the powders with large specific surface areas ($S_p > 100$ m^2 g^{-1}) and for
gels. The same conclusion has been drawn by Egorov et al. [2,3,18] who state
that the SiO_2 samples with larger specific surface areas have lower heats of
immersion and vice versa. Taylor and Hockey [19] have shown that the heat
of immersion in water of the thermally treated amorphous SiO_2 does not
depend on the specific surface areas of the powders. For these investigations,

the authors [19] used samples with specific surface areas in the range 8.5–147.5 $m^2 g^{-1}$. They also noted that the heats of immersion in water of the crystal SiO_2 modifications are probably greater than those of the amorphous samples. This assumption is supported by Wade et al. [16].

The quoted literature data indicate that the heat of immersion in water of SiO_2 powders depends on the following parameters: the structure, porosity, surface hydration, impurities, immersion temperature, and thermal treatment, as well as on the environment during the thermal treatment.

EXPERIMENTAL

Apparatus

The heat of immersion (ΔH_i) values were determined at 298 K by means of a differential type calorimeter. Details of the calorimeter are described elsewhere [20]. At least two electrical calibrations were performed before and after each experiment. All the ΔH_i values reported are the result of six or more independent determinations. The total experimental error was about ±3%. Specific surface areas of the silicas were measured by a Ströhlein area meter using the single-point nitrogen adsorption method. The X-ray patterns of the silica samples were obtained using a Siemens Kristalloflex 4 instrument with Cu K_α radiation and an Ni filter.

Materials

The silica powder was prepared by coagulation of colloidal silica using a procedure fully described elsewhere [21]. The silica powder (previously dried in an air oven at 383 K for 24 h) was heated in air for 4 h at temperatures of

TABLE 1

Specific surface areas and the water contents of SiO_2 samples

Pretreatment temperature (K)	Water loss (wt%)	Water content (wt%)	S_p ($m^2 g^{-1}$)
383	–	7.00	140
493	0.65	6.35	211
573	1.20	5.80	206
673	1.75	5.25	211
873	3.10	3.90	214
1073	4.75	2.25	208
1273	6.25	0.75	12
1373	7.00	0.00	–
1473	6.97	0.00	–

493, 573, 673, 873, 1073, 1273, 1373 and 1473 K. Water contents of these silica samples at the given treatment temperatures were estimated from the sample-mass loss after annealing. The specific surface areas and the water contents of SiO_2 samples as a function of the treatment temperature are summarized in Table 1.

The SiO_2 powders with a certain amount of the sorbed alkali metal ions were also used. A detailed report on the mode of preparation and gas–solid chromatographic properties of these alkali-metal modified silicas are given elsewhere [21]. The specific surface area and metal-ion uptake of each sample was: unmodified silica (SiO_2–H), 239 m^2 g^{-1}; silica modified with LiCl (SiO_2–Li), 204 m^2 g^{-1}, 0.12 mmol Li$^+$/g SiO_2; silica modified with NaCl (SiO_2–Na), 152 m^2 g^{-1}, 0.35 mmol Na$^+$/g SiO_2; silica modified with KCl (SiO_2–K), 159 m^2 g^{-1}, 0.27 mmol K$^+$/g SiO_2; and silica modified with CsCl(SiO_2–Cs), 124 m^2 g^{-1}, 0.45 mmol Cs$^+$/g SiO_2.

RESULTS AND DISCUSSION

The influence of thermal treatment on the specific surface area of SiO_2 is illustrated in Fig. 1. As can be seen the specific surface area of the SiO_2 sample remains constant in the temperature range 473–1073 K. This is quite as expected, bearing in mind the purity of the SiO_2 samples. The presence of cationic impurities, even in a concentration of a few tenths of a ppm, greatly affects the specific surface area during the thermal treatment. The present results are in agreement with those of Kondo and co-workers [11,22,23] and Bazhan et al. [24] who discussed the influence of impurities on the specific surface area of the thermally treated SiO_2.
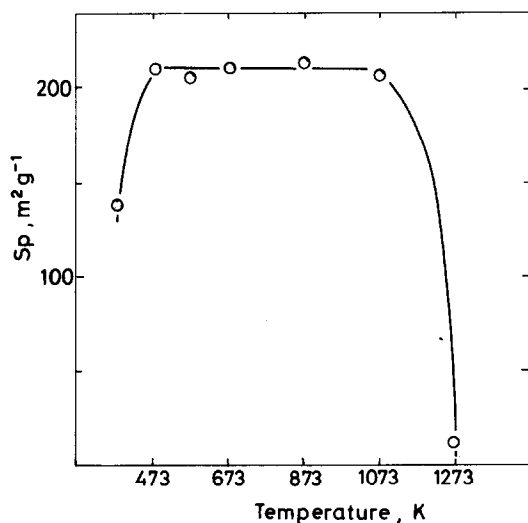

Fig. 1. Relation between the specific surface area of silica and the heat treatment temperature.

The lower value for the specific surface area of the SiO_2 sample treated at 383 K can be ascribed to the influence of the adsorbed molecular water. It is well-known that the removal of the adsorbed molecular water from the SiO_2 surface is impossible at temperatures under 473 K. Accordingly, the water present in this form blocks a part of the SiO_2 surface preventing the nitrogen molecules from reaching it.

The heats of immersion of SiO_2 in water as a function of the pretreatment temperature are shown in Table 2.

The time needed for immersion, i.e., complete evolution of the heat during immersion, did not exceed 3–5 min which is in accordance with the findings of other authors [3,4,7,18,25,26]. It should be mentioned here that only the literature data indicating a possible duration of the heat evolution during immersion of several hours (especially in the case of the immersion of Al_2O_3 samples) were reported by Guderjahn et al. [27]. The recent results of Griffiths and Fuerstenau [26] on the heat of immersion of alumina, however, show that the heat evolution was completed after approximately 3 or 4 min.

It can be seen from Table 2 that the heat of immersion of SiO_2 samples is independent of the treatment temperature in the region 483–873 K. It is also evident that the dependence of $-\Delta h_i (-\Delta H_i)$ on the treatment temperature does not have a pronounced maximum. Namely, as is stated in the Introduction, it had been thought until recently that the dependence of the heat of immersion of SiO_2 powders in water on the treatment temperatures must have a maximum at $T \approx 573$ K. This maximum will appear only if the SiO_2 samples are thermally treated in vacuum. The recent investigations of Tyler et al. [7] as well as of Kondo et al. [11] are in agreement with the present results.

Kondo et al. [11] have shown that the lowest values for the heats of immersion of SiO_2 in water are obtained for the SiO_2 samples containing minimum impurities. Table 3 presents the results of the measured heats of

TABLE 2

Heats of immersion of silica in water (as a function of the pretreatment temperature) at 298 K

Pretreatment temperature (K)	$-\Delta H_i (J\ g^{-1})$	$-\Delta h_i (mJ\ m^{-2})$
383	20.63	147
483	22.05	104
573	21.11	102
673	21.08	100
873	21.54	101
1073	18.78	90
1273	2.64	220 [a]

[a] This value can be accepted conditionally because of the error ($\pm 15\%$) in determining the $-\Delta H_i$ and S_p values.

TABLE 3

Influence of the amount of ion impurity and the environment during heat treatment on the heat of immersion of silica gel [11]

Environment during the heat treatment and the amount of ion impurity	$-\Delta h_i$ [a] $(mJ\ m^{-2})$
Vacuum, 40 ppm Na^+	137
Air, 350 ppm Na^+	108
Air, 40 ppm Na^+	97

[a] The values for $-\Delta h_i$ were obtained from ref. 11 (Fig. 4) and are related to silica gel with 2 OH nm^{-2}.

immersion as a function of the mode of the treatment and the content of Na^+ ions in the SiO_2 samples. The $-\Delta h_i$ values obtained fully correspond to the values for the heats of immersion of SiO_2 treated in air.

In order to investigate the influence of the sorbed alkali metal ions on the $-\Delta H_i (-\Delta h_i)$ values the heat of immersion of the modified SiO_2 (SiO_2–Me) samples was also measured. In Fig. 2 the dependence of the specific surface area of the SiO_2–Me samples on the amount of the sorbed Me^+ ions is given. The linear dependence obtained shows that the specific surface area of the modified SiO_2 samples depends only on the amount of the sorbed Me^+ ions and not on the type of the ions. The recently published results of Bazhan et al. [24] also suggest that the change of the specific surface area of silica gel is independent of the nature of the alkali metal cations.

The values obtained for the heats of immersion of SiO_2–Me samples in water are given in Table 4. Presentation of the heats of immersion of these samples as a function of the specific surface areas (Fig. 3) reveals a linear dependence. Due to the amount of the sorbed ions, this dependence is to be
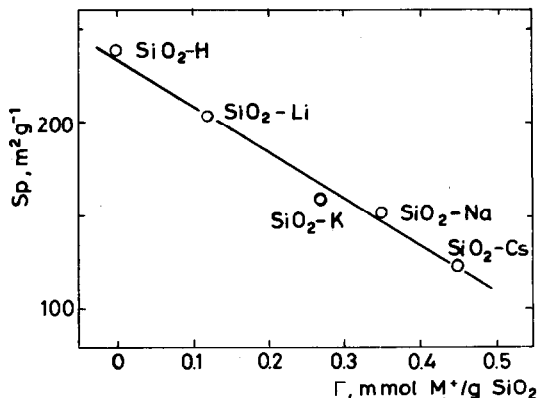

Fig. 2. The specific surface areas of metal modified silicas as a function of the amount of the sorbed metal ions.

TABLE 4

Heats of immersion of metal modified silica in water at 298 K

Type of silica	$-\Delta H_i (\text{J g}^{-1})$	$-\Delta h_i (\text{mJ m}^{-2})$
SiO_2–H	22.15	93
SiO_2–Li	18.33	90
	19.29 [a]	95 [a]
SiO_2–Na	14.78	97
SiO_2–K	16.04	101
SiO_2–Cs	12.41	100

[a] The value is related to the heat of immersion of SiO_2–Li in 0.01 mol l^{-3} HCl.

expected since the contribution of the hydration heat of Me^+ ions is negligible with regard to the contribution of the remaining H^+ ions.

The experimental results (Tables 2 and 3) indicate that the heats of immersion per unit surface area ($-\Delta h_i$, mJ m^{-2}) are independent of the specific surface area of the SiO_2 samples in the investigated region (125–240 m^2 g^{-1}). Such a conclusion is in agreement with the results of Tayler and Hockey [19] who have also found that the heat of immersion per unit surface area of the SiO_2 sample in water does not depend on the particle size.

Investigation of the thermal-treatment influence on the change of the crystal structure of the SiO_2–H samples has been carried out by the X-ray method. Untreated SiO_2–H samples have an amorphous structure. Appearance of diffraction lines at 1573 K indicates the change of the amorphous
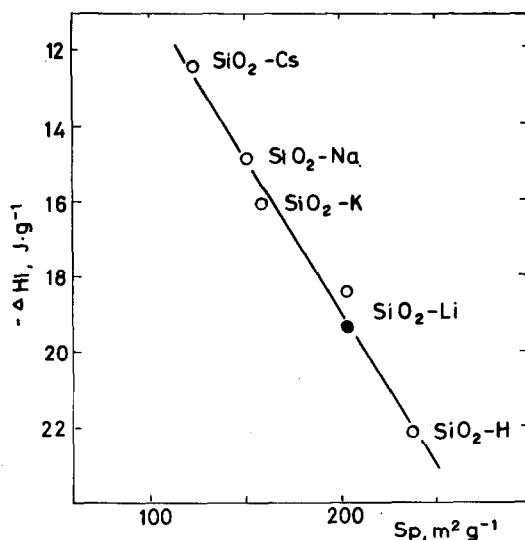

Fig. 3. Heats of immersion of alkali-metal modified silicas in water at 298 K as a function of the specific surface areas.

structure into the crystal one, more precisely, into an α-cristobalite (low-temperature modification). A complete transformation takes place at a temperature of 1573–1673 K (Fig. 4).

Such a behaviour of the amorphous silica, according to the best of our knowledge, has not been reported in the literature so far. The available literature data show that the structure change from the amorphous to the crystal state occurs at a temperature 1273 K [22,23,28]. Kondo et al. [22,23] studied the influence of impurities and pH of the solution on the structure change of the thermally treated silica gel. They concluded that the change of the amorphous into the crystal structure depends on the type and the concentration of cations and is independent of the type of anions present as impurities. For example, the change of the amorphous structure into the α-cristobalite takes place at 973 K for an Na^+ ion concentration of 870 ppm. For the same Na^+ ion content and at a treatment temperature of 1273 K the change of the amorphous structure into α-cristobalite, β-cristobalite and
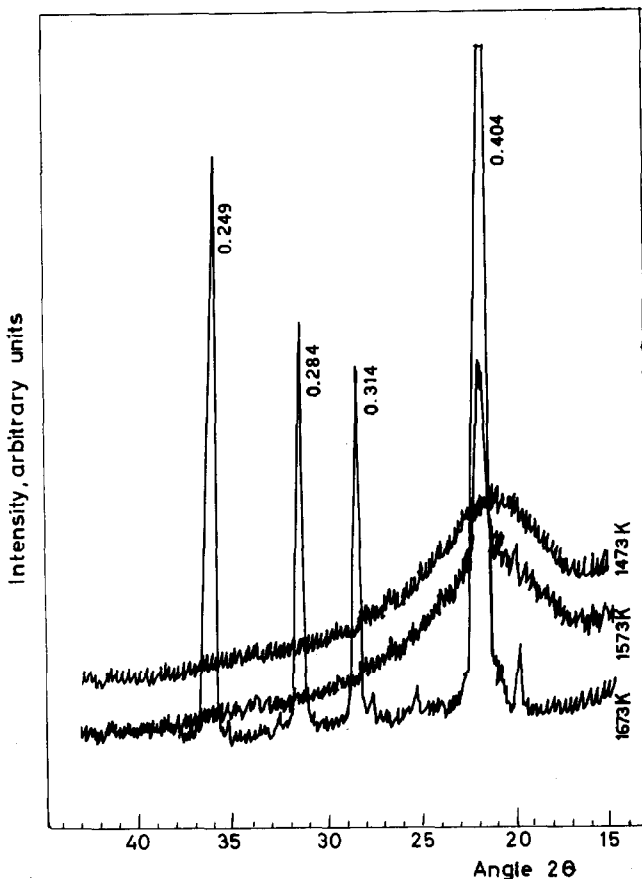

Fig. 4. X-ray powder diffraction lines of silica heated at various temperatures (numbers above peaks indicate distance, nm, between the crystal planes).

α-quartz is observed. These authors also stated that if the content of Na^+ ions is lower than 100 ppm the crystallization of silica gel at these temperatures will not occur. Unfortunately, there is no information on the temperatures at which this change takes place. Investigating the gas-chromatographic behaviour of porasil thermally treated at different temperatures, Feltl et al. [28] concluded that the partial crystallization takes place at 1173 K. Complete crystallization and the change of the amorphous structure into the α-cristobalite have been observed at 1283 K.

The high temperature for the transformation of the amorphous into the crystal structure, for the SiO_2–H samples used, was reached owing to the high purity of these samples and, perhaps, also owing to the shape of the primary particles of the material. Namely, it is known [29], that the particles of colloidal silica (the material from which the powders were obtained) have a spherical shape.

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REFERENCES

1 S.K. Milonjić, Ph.D. Thesis, University of Belgrade, Belgrade, 1981.
2 M.M. Egorov, K.G. Krasilnikov and E.A. Sysoev, Dokl. Acad. Nauk, SSSR, 108 (1956) 103.
3 M.M. Egorov, V.F. Kiselev, K.G. Krasilnikov and V.V. Murina, Zh. Fiz. Khim., 33 (1959) 65.
4 A.C. Makrides and N. Hackerman, J. Phys. Chem., 63 (1959) 594.
5 J.W. Whalen, in R.F. Gould (Ed.), Solid Surfaces and the Gas–Solid Interface, Advanced Chemistry Series, No. 33, American Chemical Society, Washington, DC, 1961, pp. 281–290.
6 T. Morimoto, K. Shiomi and H. Tanaka, Bull. Chem. Soc. Jpn., 37 (1964) 392.
7 A.J. Tyler, J.A.G. Taylor, B.A. Pethica and I.A. Hockey, Trans. Faraday Soc., 67 (1971) 483.
8 R. Sh. Mikhail, A.M. Khalil and S. Nashed, Thermochim. Acta, 24 (1978) 383.
9 A.M. Khalil, J. Colloid Interface Sci., 66 (1978) 509.
10 G.J. Young and T.P. Bursh, J. Colloid Sci., 15 (1960) 361.
11 S. Kondo, H. Fujiwara, T. Ichii and I. Tsuboi, J. Chem. Soc., Faraday Trans. 1, 75 (1979) 646.
12 S. Brunauer, D.L. Kantro and C.H. Weise, Can. J. Chem., 34 (1956) 1483.
13 L.G. Ganichenko, V.F. Kiselev, K.G. Krasilnikov and V.V. Murina, Zh. Fiz. Khim., 35 (1961) 1718.
14 T.S. Egorova, Yu.A. Zarifyants, V.F. Kiselev, K.G. Krasilnikov and V.V. Murina, Zh. Fiz. Khim., 36 (1962) 1458.

15 V.F. Kiselev, Poverkhnostnye yavleniya v poluprovodnikakh i dielektrikakh, Nauka, Moscow, 1970.

16 W.H. Wade, H.D. Cole, D.E. Meyer and N. Hackerman, in R.F. Gould (Ed.), Solid Surfaces and the Gas–Solid Interface, Advanced Chemistry Series, No. 33, American Chemical Society, Washington, DC, 1961, pp. 35–41.

17 W.H. Wade and N. Hackerman, in R.F. Gould (Ed.), Contact Angle, Wettability and Adhesion, Advanced Chemistry Series, No. 43, American Chemical Society, Washington, DC, 1964, pp. 222–231.

18 M.M. Egorov and V.F. Kiselev, Zh. Fiz. Khim., 36 (1962) 318.

19 J.A.G. Taylor and J.A. Hockey, J. Phys. Chem., 70 (1966) 2169.

20 S.K. Milonjić, M.M. Kopečni and R.A. Djerki, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 21 (1978) 1144.

21 M.M. Kopečni, R.J. Laub and S.K. Milonjić, Anal. Chem., 52 (1980) 1032.

22 S. Kondo, F. Fujiwara and M. Muroya, J. Colloid Interface Sci., 55 (1976) 421.

23 M. Muroya and S. Kondo, Bull. Chem. Soc. Jpn., 43 (1970) 3453.

24 O.V. Bazhan, V.B. Fenelonov, D.V. Tarasova and G.N. Kustova, Koloidn. Zh., 41 (1979) 1043.

25 S. Partyka, F. Rouquerol and J. Rouquerol, J. Colloid Interface Sci., 68 (1979) 21.

26 D.A. Griffiths and D.W. Fuerstenau, J. Colloid Interface Sci., 80 (1981) 271.

27 C.A. Guderjahn, D.A. Paynter, P.E. Berghausen and R.J. Good, J. Phys. Chem., 63 (1959) 2066.

28 L. Feltl, P. Lutovsky, L. Sosnova and E. Smolkova, J. Chromatogr., 91 (1974) 321.

29 R.K. Iler, in E. Matijević (Ed.), Colloidal Silica in Surface and Colloid Science, Vol. 6, Interscience, New York, 1973, pp. 1–100.