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Surface free energy components of silica gel determined by the thin layer wicking method for different layer thicknesses of gel

LUCYNA HOŁYSZ
Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, 20-031 Lublin, Poland

The influence of the thickness of silica gel layer on the penetration rate of selected liquids and, in consequence, on the value of surface free energy components determined by thin layer wicking method was studied. Plates of the following gel thickness were used: 0.25, 0.5, 1.0 and 2.0 mm. Measurements of the penetration rate of apolar liquids, i.e. three alkanes: octane, nonane and decane, diiodomethane, α-bromonaphthalene and two polar liquids: water and formamide were made for this purpose. From the obtained relationships $x^2 = f(t)$ the suitability of Washburn's equation in the whole penetration range (9 cm) was confirmed for all thicknesses of porous layers. However, the penetration rate of probe liquids changed with the thickness of the deposited layer, it was mainly dependent on an effective (apparent) radius of the interparticle pores. Using these results and the appropriate form of Washburn's equation surface free energy components of silica gel 60 (for four thicknesses of layer) were calculated. It was found that values of apolar Lifshitz–van der Waals ($\gamma_s^{LW} = 41.7 \pm 0.9\ \mathrm{mJ\,m^{-2}}$) and polar acid–base ($\gamma_s^{AB} = 11.5 \pm 0.5\ \mathrm{mJ\,m^{-2}}$): electron donor ($\gamma_s^- = 50.8 \pm 0.9\ \mathrm{mJ\,m^{-2}}$) and electron acceptor ($\gamma_s^+ = 0.7 \pm 0.1\ \mathrm{mJ\,m^{-2}}$) components of surface free energy were very similar for different layer thicknesses. Even in the case of a 2 mm thick layer reproducible values of both Lifshitz–van der Waals and acid–base component were obtained. It is important when the thin layers are prepared in laboratory conditions, i.e. from suspensions by water evaporating, and the deposited layer is of less controlled thickness. When diiodomethane and α-bromonaphthalene are considered as weakly polar liquids, the value of Lifshitz–van der Waals component of silica gel is very close to γ_s^{LW} determined from *n*-alkanes.

1. Introduction

Silica gels, belonging to porous oxide adsorbents, have been most widely used and described [1–18]. This popularity results from its application in extraction, filtration and catalysis (catalysts and catalyst carriers), and as adsorbents used in chromatography, media drying gases and solvents, crystal nuclei for water solidification, ion exchangers etc. [2]. Easy production of this adsorbent and possible modification of its surface properties, geometric structure of pores and character of chemical surface are relevant.

Silica gel can occur in various forms; however, they show similar surface properties as porous glass, quartz as well as silicate and siloxane crystals [9]. A common feature of these compounds is the occurrence on their surface of functional hydroxyl groups bonded with the skeleton by covalent bonds. Silanol groups can exist on the surface as single, geminal and vicinal groups which can form so-called bounded pairs. They are considered as strong adsorption sites [10–13] owing to specific interactions with adsorbate particles able to form hydrogen bonds, or generally donor–acceptor bonds. Thermal treatment of the surface causes removal of hydroxyl groups from gel surface, and its hydrophilic properties change due to the formation of siloxane bonds [7]. This leads to hydrophobization of the surface [11] and thereby to decreased adsorption activity and adsorption magnitude [6].

For a long time hydroxyl groups have been considered as the only active adsorption sites [11], although some authors suggested also the existence of the so-called "strained" siloxane bridges [14–18]. Siloxane bridges occurring on the surface are usually hydrophobic [1].

Bonds (σ) existing in Si–O–Si group are strained due to interactions of d_π–p_π (weaker than typical p_π–p_π bond), and both free electron pairs appearing on oxygen atom participate in π back bonding, which means that siloxane sites cannot form hydrogen bonding with adsorbates [1, 5].

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The studies of water adsorption on silica carried out by Fink and Camara [17] using the method of i.r. spectroscopy have shown that at low coverage water molecules are not adsorbed on hydroxyl groups but on aprotonic sites. Their structures suggest that some silica atoms present in adsorption sites ("strained" siloxane bridges) can have their co-ordination number equal 5, which indicates that adsorption at aprotonic sites takes place due to the formation of co-ordination bonds [17].

Also the studies of Knözinger and Stählin [18] present experimental evidence for the existence of aprotonic sites on silica surface. By the gravimetric method and infrared spectroscopy they studied adsorption of tertiary butanol and of di-isopropylether on silica of various density of hydroxyl groups. Adsorption of molecules of these liquids is a complex process and leads to the formation of compounds containing hydrogen and coordination bondings, the centers of which are "strained" siloxane bridges.

Despite an extensive literature about silica gels [1–18], its surface properties and structure still hide many secrets. Taking the above considerations into account the purpose of this paper, besides determination of the magnitude of surface silica gel interactions (apolar of Lifshitz–van der Waals type and acid–base polar of Lewis) [19–25], was to examine the effect of porous layer thickness of a solid on the penetration rate of probe liquids and thereby on the values of thus calculated surface free energy components, using the method of thin layer wicking [27–33]. According to the approach of van Oss *et al.* [19–25], surface free energy, γ, of a liquid or solid can be expressed by two components

$$\gamma = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \tag{1}$$

where γ^{LW} is the apolar component which results from Lifshitz–van der Waals (London dispersion, Debye induction and Keesom orientation forces), γ^{AB} is the polar component which results from complementary acid–base interactions (electron donor, γ^-, and electron acceptor, γ^+). As dipole–dipole interactions are slight due to their mutual compensation, their involvement in surface free energy is small (about 2%) and can be omitted. Accordingly the component γ^{LW} results largely from dispersive interactions of London [26].

Interactions γ^{AB} occur most often as a result interactions of hydrogen bonding and can be expressed by the relationship

$$\gamma^{\mathrm{AB}} = 2(\gamma^-\gamma^+)^{1/2} \tag{2}$$

According to this approach interactions of solid–liquid interface can be expressed by the equation

$$\begin{aligned}\gamma_{\mathrm{sl}} = {} & [(\gamma_{\mathrm{s}}^{\mathrm{LW}})^{1/2} - (\gamma_{\mathrm{l}}^{\mathrm{LW}})^{1/2}]^2 + 2[(\gamma_{\mathrm{s}}^+\gamma_{\mathrm{s}}^-)^{1/2} + (\gamma_{\mathrm{l}}^+\gamma_{\mathrm{l}}^-)^{1/2} \\ & - (\gamma_{\mathrm{s}}^+\gamma_{\mathrm{l}}^-)^{1/2} - (\gamma_{\mathrm{s}}^-\gamma_{\mathrm{l}}^+)^{1/2}]\end{aligned} \tag{3}$$

From Equation 3 it is possible to determine the components $\gamma_{\mathrm{s}}^{\mathrm{LW}}$, γ_{s}^+ and γ_{s}^- of surface free energy using, e.g. the method of thin layer wicking and three liquids with known components of their surface tension.

2. Experimental procedure

2.1. Materials

Commercial silica gel 60 plates for thin layer chromatography (TLC) and preparative liquid chromatography (PLC) (without fluorescent indicator), Merck, of following silica gel thicknesses: 0.25, 0.5, 1.0 and 2.0 mm were used in the studies. Plates of dimensions 2.5 × 10 cm obtained from 20 × 20 cm plates were used for measurements. To remove water physically adsorbed on silica surface [31], the plates were dried for 2 h at 150 °C and then kept in a desiccator containing molecule sieves (4A + 5A) previously heated at 400–450 °C. For measurements of the penetration rate the following liquids were used: *n*-octane, *n*-nonane and *n*-decane (pure, Reachim), α-bromonaphthalene, diiodomethane (analytical pure, POCh Gliwice), formamide (pure for chromatography, Belgium), diionized water (Millipore).

2.2. Method

Thin-layer wicking method is based on liquid penetration in porous solid layer deposited on a glass plate or powdered solid packed in a glass capillary. The liquid penetration rate is described by Washburn equation [27–30]. A 15 × 7 cm chromatographic chamber DS (Chromdes, Medical University, Lublin) of sandwich type was used for measurements. It consists of a flat Teflon plate with several gutters, two of which are liquid containers. The examined plate was placed on thresholds with the gel layer downward, and the front of the penetrating liquid was observed through a glass plate. The whole chamber was covered with a glass plate.

All measurements of penetration rate were carried out at 20 °C for each kind of plate in two series: with bare surface and precontacted with liquid vapours to form adsorption film (duplex film) of the liquids studied. For each liquid three to six measurements of penetration rate were made. The details of thin layer wicking measurements were described elsewhere [28–30].

3. Results and discussion

As mentioned in the experimental section, measurements of the penetration rate of probe liquids were carried out for four thicknesses of silica gel layer. Straight line relationships $x^2 = f(t)$ were obtained for all four coverings; therefore, example results of liquid penetration in porous layer of silica gel 60 of 0.25 mm in thickness have been presented in Figs. 1–3. Because the penetration time is actually measured, the obtained relationships have been presented as function $t = f(x^2)$. Fig. 1 shows penetration rate of three alkanes: *n*-octane, *n*-nonane and *n*-decane as a function of the squared distance (to 9 cm) for plates earlier contacted with a saturated vapour of these alkanes (curves 1p–3p) and for bare plates (curves 1b–3b). For each case three to six experiments were made and standard deviations were marked on the curves. As can be seen, there is a very good reproducibility of

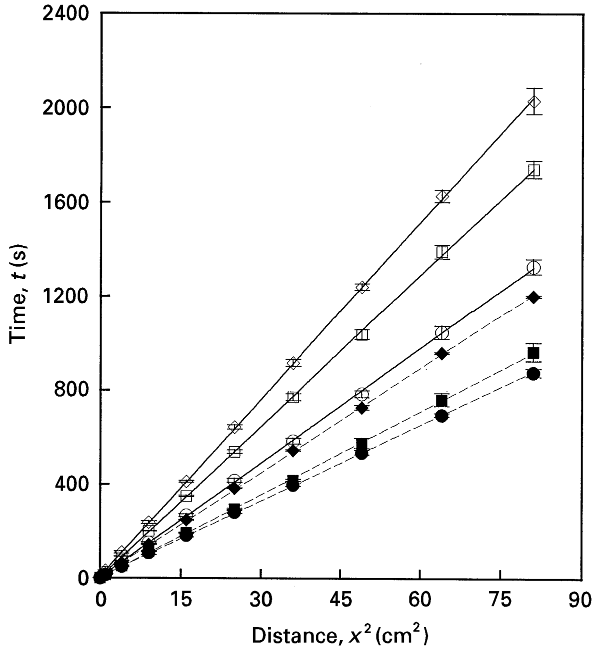

Figure 1 Penetration time of *n*-alkanes (lines: 1p (●), 1b (○) octane; 2p (■), 2b (□) nonane; 3p (◆), 3b (◇) decane) into silica gel 60 layer 0.25 mm thickness for precontacted surface (-----) and bare surface (———) versus squared distances.

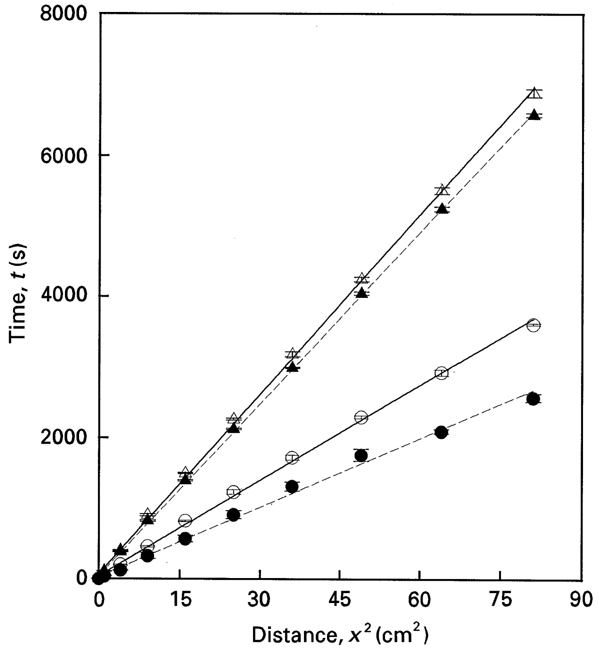

Figure 2 Penetration time of diiodomethane (lines 1p (●), 1b (○)) and α-bromonaphthalene (lines 2p (▲), 2b (△)) into silica gel 60 layer 0.25 mm thickness for precontacted surface (dashed line) and bare surface (solid line) versus squared distances.

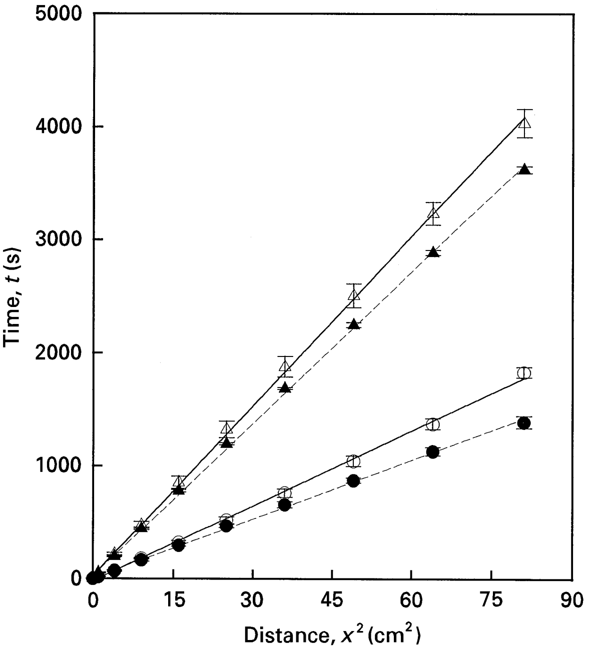

Figure 3 The same relationship as in Fig. 2, but for water (lines 1p (●), 1b (○)) and formamide (lines 2p (▲), 2b (△)).

experiments up to a distance of 9 cm. The linear relationship has been presented by linear regression, using the method of least squares.

From the results shown in Fig. 1 (curve 1p–3p) and on the basis of the classical form of Washburn equation, in which the capillary radius r was replaced by the effective (apparent) radius R of the interparticle pores in the porous layer of the solid

$$x^2 = \frac{Rt}{2\eta}\gamma_1 \qquad (4)$$

where t is the time of liquid penetration at a distance x, η is the liquid viscosity, the effective radius of the interparticle pores of silica gel layer can be determined [28–30]. When a liquid totally wets the solid surface which was previously in equilibrium with saturated vapour of the liquid (precontacted surface p), the change of free energy, ΔG, on replacing solid–gas interface by liquid–solid interface, is equal to the liquid surface tension, i.e. $\Delta G = \Delta G_p = \gamma_1$ [28–30]. During liquid penetration along the plate ΔG does not change, which results from straight linear relationship $x^2 = f(t)$ and confirms the suitability of Washburn's equation for a given system.

From the penetration measurements made earlier for 12 alkanes (from pentane to hexadecane) on silica plates [33] it was found that octane, nonane and decane (taking into account volatility and viscosity (Equation 4) gave the most compatible values of both the effective radius and apolar component of gel surface free energy. Pentane evaporates too fast from gel layer (decreased temperature, lack of viscosity control); therefore, penetration rate for the plate contacted with this hydrocarbon cannot be measured. The effective radius for hexane and heptane differs from this parameter determined for octane, nonane and decane [33].

From the results presented in Fig. 1 (curves 1p–3p) and on the basis of the surface tension values of alkanes and their viscosity (Table I) the effective radius of interparticle pores formed in porous silica gel layer was calculated and the results are given in Table II. As can be seen, for octane a smaller value of R was obtained. It is possible that during penetration process this hydrocarbon partially evaporates from the surface, which may result in a smaller R value. The calculated average value of the effective radius from three alkanes R_{Av} is $5.015 \pm 0.345 \times 10^{-5}$ cm. Also the average radius determined for two alkanes: nonane

TABLE I Values of the surface tension, γ_1, and its components, Lifshitz–van der Waals, γ_1^{LW}, electron acceptor, γ_1^+, electron donor, γ_1^- (in $mN\,m^{-1}$), viscosity at 20 °C (in cP) and boiling point (°C) of probe liquids taken from the literature [20,21,35,36]

Liquid	γ_1	γ_1^{LW}	γ_1^+	γ_1^-	η	T_b
n-Octane	21.8	21.8	0	0	0.542	125
n-Nonane	22.9	22.9	0	0	0.714	151
n-Decane	23.9	23.9	0	0	0.920	174
CH_2J_2-D	50.8	50.8	0[a] 0.72[b]	0[a] 0[b]	2.821	181R
α-Bromonaphthalene-B	44.4	44.4[a] 43.6[b]	0[a] 0.4[b]	0[a] 0.4[b]	4.890	281
Water	72.8	21.8	25.5	25.5	1.002	100
Formamide	58.0	39.0	2.28	39.6	3.783	193R

[a] from [21].
[b] from [20].

TABLE II Lifshitz–van der Waals component of surface free energy (in $mJ\,m^{-2}$) of silica gel 60 for layer thickness 0.25 mm determined from different values of effective (apparent) radius *R* of the interparticle pores in the layer of the silica gel

Liquid	$R \times 10^{-5}$ cm	γ_s^{LW}	$R_{av} \times 10^{-5}$ cm	γ_s^{LW}	$R_{Av(9,10)} \times 10^{-5}$ cm	γ_s^{LW}
octane	4.624	38.6	5.015	37.1	5.210	36.5
nonane	5.278	36.5	5.015	38.1	5.210	37.5
decane	5.142	40.1	5.015	40.5	5.210	39.8
Average	5.015 ± 0.345	38.4 ± 1.8	–	38.6 ± 1.7	–	37.9 ± 1.7

R for particular *n*-alkane, R_{Av} average from three alkanes and $R_{Av(9,10)}$ average from two alkanes: nonane and decane.

and decane, $R_{Av(9,10)} = 5.210 \pm 0.096 \times 10^{-5}$ cm is given in Table II. In calculations of Lifshitz–van der Waals component all three values of radius (R, R_{Av} and $R_{Av(9,10)}$) were used. To calculate γ_s^{LW} the results given in Fig. 1 (curves 1b–3b) were used, i.e. the penetration rate of octane, nonane and decane on bare silica gel 60 surface. As it appears the penetration time of the same distance *x* is longer than in the case of the surface covered with duplex film (Fig. 1), when surface free energy is decreased by film π_e pressure, i.e. $\gamma_{sv} = \gamma_s - \pi_e$. As *n*-alkanes totally wet solid surface ($\Delta G > 0$) the replacement of solid–gas interface by solid–liquid interface and a bulk liquid is accompanied by the following change of free energy

$$\Delta G_b = \frac{2\eta x^2}{Rt} = \gamma_s - \gamma_{sl} - \gamma_1$$

$$= W_A - W_C = 2(\gamma_s^{LW}\gamma_1^{LW})^{1/2} - 2\gamma_1 \quad (5)$$

Hence

$$\gamma_s^{LW} = \left[\frac{\Delta G_b + 2\gamma_l}{2(\gamma_l^{LW})^{1/2}}\right]^2 \quad (6)$$

In Table II are given the values of γ_s^{LW} component of silica gel calculated using previously determined parameter *R*. As can be seen the γ_s^{LW} values calculated both for *R* (particular hydrocarbon) and R_{Av} (average radius of three alkanes) and $R_{Av(9,10)}$ (of nonane and decane) do not practically differ: $\gamma_s^{LW} = 38.4 \pm 1.8$, 38.6 ± 1.7, $37.9 \pm 1.7\ mJ\,m^{-2}$. Thus in further calculations average radius determined from penetration of three alkanes was applied for estimation of surface free energy components.

In the case of liquids which form a defined contact angle on solid surface the situation becomes more complicated. From the previous studies it results that the dynamic contact angle occurring during liquid penetration is not equal to the static angle from Young equation [28,30,33]. As Blake and Haynes [37] have shown, the dynamic contact angle differs from the static one; however, the receding dynamic contact angle equals the static one if the liquid totally wets the solid surface.

Accordingly, it was concluded from theoretical considerations based on experimental results for liquids which form a contact angle on the solid surface [28–30,33] that the difference between the calculated energy change for bare surface, ΔG_b, and for that covered with film (precontacted), ΔG_p, is equal to the difference between the work of adhesion, W_A, and that of liquid cohesion, W_C

$$\Delta G_b - \Delta G_p = W_A - W_C \quad (7)$$

Hence in the case of apolar liquid

$$\Delta G_b - \Delta G_p = 2(\gamma_s^{LW}\gamma_1^{LW})^{1/2} - 2\gamma_1 \quad (8)$$

and in the case of polar liquid

$$\Delta G_b - \Delta G_p = 2(\gamma_s^{LW}\gamma_1^{LW})^{1/2} + 2(\gamma_s^-\gamma_1^+)^{1/2} + 2(\gamma_s^+\gamma_1^-)^{1/2} - 2\gamma_1 \quad (9)$$

Diiodomethane and α-bromonaphthalene are liquids which show high surface tension (Table I) and form a contact angle on the solid surface. Despite the fact that diiodomethane shows a slight electron acceptor-parameter $\gamma_1^+ = 0.72\ mN\,m^{-1}$, and α-bromonaphtalene also electron donor one, $\gamma_1^+ = \gamma_1^- = 0.4\ mN\,m^{-1}$, in the first approximation they can be treated as apolar liquids [20,21]. Nevertheless, in further calculations of surface free energy components two cases were taken into account: as totally apolar liquids [20] and with consideration of small acid–base parameter [21].

Fig. 2 presents the penetration rate of diiodomethane and α-bromonaphthalene for plates of 0.25 mm thickness of bare silica gel layer (solid line) and precontacted with these liquids (dashed line), and Fig. 3 – analogous relationship only for two polar liquids: water and formamide. Table III presents the calculated values of surface free energy components of silica gel, determined from Equations 8 and 9. Treating with diiodomethane and α-bromonaphthalene as apolar liquids, Lifshitz–van der Waals component of surface free energy determined by using these liquids is $\gamma_s^{LW} = 41.7\,\mathrm{mJ\,m^{-2}}$ and $43.4\,\mathrm{mJ\,m^{-2}}$, and additionally by using $\gamma_s^{LW} = 38.6\,\mathrm{mJ\,m^{-2}}$ determined from three alkanes, the average value of $\gamma_s^{LW} = 41.2 \pm 2.4\,\mathrm{mJ\,m^{-2}}$.

The obtained γ_s^{LW} values were used in further studies to obtain acid–base components of surface free energy. For studied a silica gel sample (0.25 mm thickness) the average value of electron donor component $\gamma_s^- = 51.3 \pm 0.3\,\mathrm{mJ\,m^{-2}}$, and electron acceptor one $\gamma_s^+ = 0.7 \pm 0.4\,\mathrm{mJ\,m^{-2}}$. Table III contains also the values of those components calculated for the particular γ_s^{LW} components, i.e. determined on the basis of alkanes, diiodomethane and α-bromonaphthalene. As it is seen all values are very similar. Applying Equation 2 the values of acid–base component, γ_s^{AB}, as well as the total surface free energy, γ_s, of silica gel were determined (from Equation 1).

In the second case, a small acid–base parameter of diiodomethane and α-bromonaphthalene were taken for calculation of surface free energy components. Table IV presents the values of the particular surface free energy components for two systems consisting of three liquids: diiodomethane, water, formamide (DWF) and α-bromonaphthalene, water, formamide (BWF). As can be noticed the value of Lifshitz–van der Waals component has considerably decreased from 41.2 to $32.8\,\mathrm{mJ\,m^{-2}}$, that gives a 20.4% difference. The value of electron donor component γ_s^- does not practically change, whereas that of electron acceptor γ_s^+ considerably increases from 0.7 to $2.5\,\mathrm{mJ\,m^{-2}}$. However, the total value of surface free energy involving all interactions does not practically change, $\gamma_s = 53.3$ and $54.9\,\mathrm{mJ\,m^{-2}}$, respectively. Thus, it can be concluded that the treatment of diiodomethane and α-bromonaphthalene as apolar liquids and then as weakly polar ones is not reflected by the total value of surface free energy, but it is significant with regard to the particular values of surface free energy components.

It seemed also interesting whether the thickness of deposited solid layer can effect the penetration rate of a liquid and in consequence the calculated values of the solid surface free energy components. Exact control of SiO_2 layer thickness was possible by using commercial plates with controlled layer thickness.

Analogous measurements, as for 0.25 mm silica gel 60, were carried out for covering layers 0.5, 1.0 and 2.0 mm thick. In Figs 4 and 5 are shown examples of the penetration rate of decane (Fig. 4) and diiodomethane (Fig. 5) on plates covered with duplex film, by contacting with saturated vapour of the liquid (dashed line) and for bare surfaces (solid line). As can be seen the penetration rate changes with the thickness of the deposited layer (0.25, 0.5, 1.0 and 2.0 mm) and mainly depends on the radius of the interparticle pores (Table V) (Equation 4), which is seen both for the plates with film (curves 2p, 1p, 4p and 3p) and bare surfaces (curves 2b, 1b, 4b and 3b). In Table V the values of effective radius *R* are presented for all silica gel thicknesses, determined for particular alkanes (octane, nonane and decane) and the average value, R_{AV}, which was used in further calculations. The values of

TABLE III Values of the Lifshitz–van der Waals, γ_s^{LW}, electron acceptor, γ_s^+, electron donor, γ_s^-, acid–base, γ_s^{AB}, components of surface free energy (in $\mathrm{mJ\,m^{-2}}$) of silica gel 60 for layer thickness 0.25 mm

γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
38.6[a]	1.1	51.0	15.1	53.6
41.7[b]	0.7	51.3	12.0	53.7
43.4[c]	0.4	51.6	9.1	52.5
41.2 ± 2.4	0.7 ± 0.4	51.3 ± 0.3	12.0 ± 3.0	53.3 ± 0.7

γ_s^{LW} calculated from
[a] *n*-alkanes
[b] diiodomethane
[c] α-bromonaphthalene.

TABLE IV Values of surface free energy components (in $\mathrm{mJ\,m^{-2}}$) of silica gel 60 for layer thickness 0.25 mm; diodomethane and α-bromonaphthalene were considered as weakly polar liquids

Liquids	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
DWF	31.5	2.8	50.1	23.7	55.2
BWF	34.0	2.1	50.4	20.6	54.6
Average	32.8 ± 1.8	2.5 ± 0.5	50.3 ± 0.2	22.2 ± 2.2	54.9 ± 0.4

D, diiodomethane; B, α-bromonaphthalene; W, water; F, formamide.

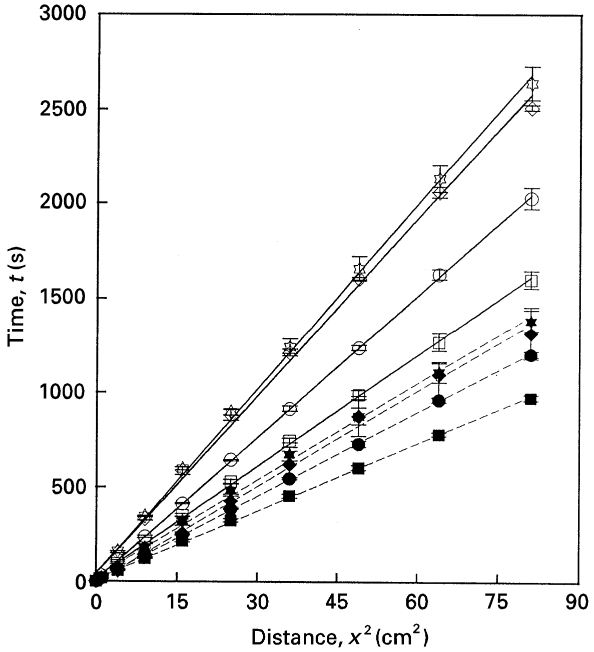

Figure 4 Penetration rate of decane on precontacted surface (-----) and bare surface (——) for different layer thicknesses of silica gel 60 versus squared distances. 2p (●), 2b (○) 0.25 mm; 1p (■), 1b (□) 0.5 mm; 4p (★), 4b (☆) 1.0 mm; 3p (◆), 3b (◇) 2.0 mm.

the particular surface free energy components for all thicknesses of silica gel layers are summarized in Table VI. The best results of Lifshitz–van der Waals component determination were obtained for all layer thicknesses studied by using *n*-alkanes and α-bromonaphthalene (standard deviation is 1.7 and 1.1 mJ m^{-2}) despite the fact that the difference between average γ_s^{LW} values was 5.0 mJ m^{-2}, which was 12.0% of the average γ_s^{LW} value – 41.7 mJ m^{-2} determined from alkanes, diiodomethane and α-bromonaphthalene. In the case of diiodomethane a higher γ_s^{LW} value was obtained for two thicknesses of SiO_2 layer 1.0 and 2.0 mm. However, the average γ_s^{LW} value (of alkanes, diiodomethane and α-bromonaphthalene) was very similar amounting 41.7 ± 0.8 mJ m^{-2}. A very good consistency for all silica gel coverings was obtained with regard to electron acceptor components $\gamma_s^{+} = 0.7 \pm 0.1$ mJ m^{-2} and electron donor ones $\gamma_s^{-} = 50.8 \pm 0.9$ mJ m^{-2}. It is difficult to find in the literature surface free energy components for silica gel determined by other methods. Nevertheless, the obtained values are confirmed in good agreement with analogous values obtained for silica [25] and fused silica [38].

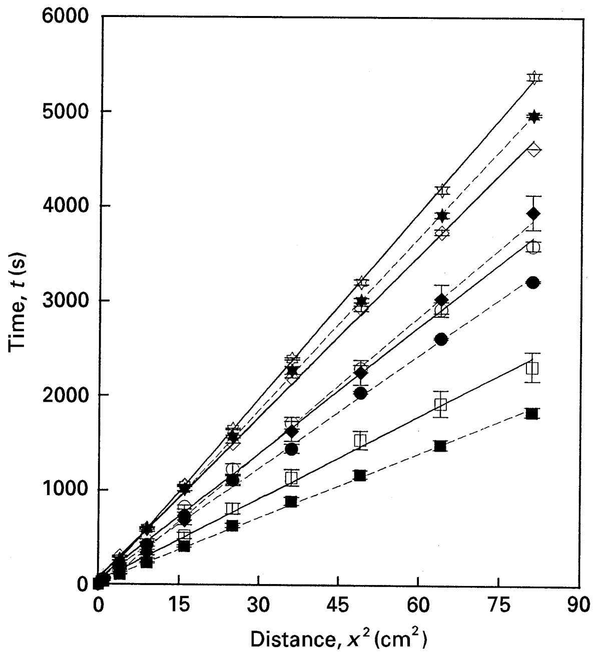

Figure 5 The same relationship as in Fig. 4, but for diiodomethane. 2p (●), 2b (○) 0.25 mm; 1p (■), 1b (□) 0.5 mm; 4p (★), 4b (☆) 1.0 mm; 3p (◆), 3b (◇) 2.0 mm.

TABLE V Values of effective (apparent) radius of the interparticle pores for different layer thicknesses of silica gel 60

Layer thickness of SiO_2 (mm)	R ($\times 10^{-5}$ cm)			R_{AV} ($\times 10^{-5}$ cm)
	octane	nonane	decane	
0.25	4.624	5.278	5.142	5.015 ± 0.345
0.5	5.933	6.370	6.310	6.204 ± 0.237
1.0	4.482	4.720	4.397	4.533 ± 0.167
2.0	5.666	5.298	4.752	5.239 ± 0.460

The average value of surface free energy of silica gel $\gamma_s = 53.3 \pm 0.8$ mJ m^{-2} is close to γ_s of quartz obtained from contact angle measurements of probe liquids [39].

Table VII shows the values of surface free energy components of silica gel 60 for different layer thicknesses when diiodomethane and α-bromonaphthalene were considered as weakly polar liquids. As can be seen, for all silica gel coverages the total value of surface free energy is practically the same as in the case when diiodomethane and α-bromonaphthalene were treated as apolar liquids (Table VI). However, differences occur between the particular components of the surface free energy (γ_s^{LW} and γ_s^{+}). The value of Lifshitz–van der Waals component of silica gel equals 33.8 ± 0.7 mJ m^{-2} (Table VII) and is very close to $\gamma_s^{LW} = 37.5$ mJ m^{-2} determined from *n*-alkanes (Table VI).

From the studies carried out it can be found that silica gel has a high value of basic component, i.e., it shows strong electron donor properties and a small value of acid component. From literature reports, it appears that silanol groups present on silica surface are strong adsorption sites of electron acceptor character [11–13]. For amorphous silica heated in vacuo at 180–200 °C, the concentration of surface hydroxyl groups per 1 nm^2 is 4.6 ± 0.1, and for samples heated at 1000 °C this amount decreases to 0.25 of OH group [7]. A pure surface can be maintained only in

TABLE VI Values of the surface free energy components (in mJ m^{-2}) of silica gel 60 for different layer thicknesses

Layer thickness of SiO_2 (mm)	γ_s^{LW}						γ_s^{LWa}	γ_s^{+}	γ_s^{-}	γ_s^{AB}	γ_s
	octane	nonane	decane	av.	D	B					
0.25	37.1	38.1	40.6	38.6 ± 1.8	41.7	43.4	41.2 ± 2.4	0.7	51.3	12.0	53.4
0.5	37.0	39.8	40.7	39.2 ± 1.9	41.2	42.6	41.0 ± 1.7	0.7	49.8	11.8	52.7
1.0	34.2	36.2	37.6	36.0 ± 1.7	49.5	43.2	42.9 ± 6.8	0.6	51.7	11.1	54.4
2.0	36.2	35.7	36.3	36.0 ± 0.3	48.2	41.0	41.7 ± 6.1	0.6	50.4	11.0	52.7
Average	36.1 ± 1.3	37.5 ± 1.9	38.8 ± 2.2	37.5 ± 1.7	45.2 ± 4.3	42.5 ± 1.1	41.7 ± 3.9	0.7 ± 0.1	50.8 ± 0.9	11.5 ± 0.5	53.3 ± 0.8

[a]average from: alkanes, D (diiodemethane) and B (α-bromonapthalene).

TABLE VII Values of the surface free energy components (in mJ m^{-2}) of silica gel 60 for different layer thicknesses; diodomethane and α-bromonaphthalene were considered as weakly polar liquids

Layer thickness of SiO_2 (mm)	DFW					BWF				
	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
0.25	31.5	2.8	50.1	23.7	55.2	34.0	2.1	50.4	20.6	54.6
0.5	31.3	2.8	48.9	23.4	54.7	33.3	2.2	49.0	20.8	54.1
1.0	38.0	1.4	51.1	16.9	54.9	34.1	2.3	50.7	21.6	55.7
2.0	37.3	1.3	49.8	16.1	53.4	31.8	2.6	49.3	22.6	54.4
Average	34.5	2.1	50.0	20.0	54.6	33.1	2.3	49.9	21.4	54.7
	± 3.6	± 0.8	± 0.9	± 4.1	± 0.8	± 1.0	± 0.2	± 0.8	± 0.9	± 0.7

conditions of high vacuum of 133×10^{-10} Pa or even lower [40]. In vacuum of 133×10^{-6} Pa so many water molecules collide with the surface that the formation of a monolayer is possible in one second. During penetration rate measurements, the studied samples contact with air, and thus water molecules, too. From the studies of Jańczuk [38], the surface properties of quartz change in natural surrounding as a function of time of the quartz sample contact with water molecules and relative air humidity. A water film of 11–15 statistical monolayers is formed on the surface, which has different properties compare to those in the bulk phase [41]. The structure of this film depends on its thickness, and it is best ordered (ice-like) in the two first water monolayers [42–44].

The determined values of work of wetting: spreading, W_s, immersional, W_I, and adhesional, W_A, for water and octane on silica surface indicate preferential SiO_2 surface wetting by water. Higher values of wetting work in water–silica system result from the formation of hydrogen bonds between water molecules and surface OH groups [45]. Various kinds of silica both porous and wide-porous with a totally hydroxylated surface adsorb the same amount of water at the same comparatively low relative pressures p/p_0. Hence it appears that surface silanol groups constitute the main and primary centres for adsorption of water molecules [7]. The first type of interactions consists in that water acts as proton donor forming hydrogen bonding with oxygen [–Si(OH)–H_2O], while in the second case acts as acceptor of protons binding by hydrogen bonding with hydrogen atom [–Si (OH)–OH_2]. The possibility of binding by both kinds of hydrogen bonding is not excluded. However, it seems that the first model is more likely [7]. This is confirmed by calculations performed by methods of quantum chemistry [46]. H_2O adsorbed as proton donor is more stable than water adsorbed as proton acceptor because the interaction energy of water molecule being of proton donor is much lower than in the case of the molecule being proton acceptor.

4. Conclusions

The results of the presented studies suggest that water can be adsorbed on silanol groups as donor of protons, which causes an increase of electron donor properties of silica gel surface. The determined properties of surface free energy components of silica gel should thus be considered in the aspect of possible changes of surface properties of this solid through the presence of adsorbed water molecules. The total value of surface free energy is very similar to the free energy of the liquid–solid interphase at a triple point for water: $\gamma_{s1} = 44.5 \pm 10\,\mathrm{mJ\,m^{-2}}$ [47] and $40.9\,\mathrm{mJ\,m^{-2}}$ [48], that can confirm these suppositions. It can be also concluded that thin layer wicking is a very useful method for determining surface free energy components, particularly for solids (powders), when contact angles cannot be measured. In the case of depositing a powder layer even up to 2.0 mm thick good results of liquid penetration are obtained, and the determined values of components are very similar and independent from thickness of the layer. This is particularly important when the thin layers are prepared in a laboratory condition, i.e. from suspensions by water evaporating, and the deposited layer is of less controlled thickness.

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