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Investigation of the effect of substrata on the surface free energy components of silica gel determined by thin layer wicking method

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The components of surface free energy of silica gel deposited on glass plates, aluminium or plastic sheets (commercial Merck's plates for TLC) were determined by applying two theoretical approaches: the Lifshitz-van der Waals acid-base approach (LWAB), the geometric mean of apolar and polar interactions approach (GM). The thin layer wicking method was applied. Besides, from the measured contact angles of probe liquid (diiodomethane, α-bromonaphthalene, water, formamide, glycerol and ethylene glycol) surface free energy components were calculated for the substrata on which the silica gel was deposited. In this case the equation of state (ES) was additional by applied. The study has shown that both the kind of substratum and that of the chambers used for measuring the penetration rate of the liquid do not influence the calculated values of the surface free energy components of silica gel. The components calculated from the two models of interfacial interactions: γ_s^{LW} and γ_s^{AB} or γ_s^d and γ_s^p appeared to be practically the same if diiodomethane and α-bromonaphthalene were considered as weakly polar liquids, i.e. donor-acceptor interactions in the surface tension were taken into account. However, when γ_l^+ and γ_l^- of these liquids are neglected, considerable differences occur, particularly in the determined value of Lifshitz-van der Waals component. The values of the total surface free energy of substrata calculated by applying three thermodynamic approaches are very similar, but if diiodomethane and α-bromonaphthalene are considered as weakly polar liquids this similarity is more distinct.

1. Introduction

Surface free energy of solids and its components are important parameters characterizing surface properties of solids and interfacial interactions. However, determination of the surface free energy components is still unresolved, because the known methods, which are based on contact angle measurements [1–5], adsorption measurements (determination of the film pressure) [6–8] or enthalpy of wetting [9–14], are indirect ones. Another important problem is interpretation of interfacial free energy. In the literature of recent years two basic approaches for the description of interfacial free energy can be found [5, 15–17]. The first is based on the assumption that surface free energy of a solid or liquid consists of components resulting from various intermolecular interactions [18–27]. The other [28, 29], although strongly criticized [15, 30–32], assumes that surface free energy does not consist of any components and therefore the interfacial free energy is a function of the total surface free energy of contacting phases only.

Considering additivity of the components, the liquid-liquid or solid-liquid interfacial free energy (γ_{12}) is described by the sum of total surface free energies (surface tensions) of both contacting phases, diminished by the work of adhesion (W_A) between these phases. According to Fowkes [19], the W_A of dispersion interactions (γ^d) can be expressed as a geometric mean, while Owens and Wendt [20], and Kaelble and Uy [21] used also the geometric mean for polar interactions (γ^p). Van Oss *et al.* [22–27] expressed the work of adhesion by the geometric mean from Lifshitz-van der Waals components (γ^{LW}), and from electron-donor (γ_1^-) and electron-acceptor (γ_2^+) (and vice versa) parameters of acid-base (γ^{AB}) interactions for two phases being in contact.

Making a comparative analysis of thermodynamic approaches Schneider [5] found that the values of surface free energy obtained from the equation of state (ES) on high and low energy substrata were not consistent with fundamental premises of the theory. According to this author [5] in the approach based on geometric mean equation (GM), underestimated values of the dispersion component of surface free energy have been obtained for most systems studied. However, the results obtained from Lifshitz-van der Waals acid-base (LWAB) are compatible with theoretical assumptions but depend on the sequence of determination of acid-base component [5]. For several cases Schneider could not determine electron-acceptor parameter because he obtained a negative square root value [5].

It appears from the studies of Jańczuk *et al.* [1–3] that for some systems similar values are obtained for the components: apolar (γ^{d} and γ^{LW}), polar (γ^{p}) and acid-base (γ^{AB}) of surface free energy using the approach based on geometric mean [20, 21] and that of van Oss *et al.* [22–27].

Berg [33] and Morra [34] had questioned the experimentally determined γ^{+} and γ^{-} parameter for PMMA and PCV, but they do not reject the approach by van Oss *et al.* [22–27]. It cannot be excluded that the real surface of these polymers may possess interactions as determined from the experiments because of the presence of adsorbed water, some impurities as well as polar functional groups resulting from technological polymerization process itself.

However, Lifshitz-van der Waals acid-base approach [22–27] seems to give a better insight into intermolecular interactions. The main problem in using this method consists in determining "true" values of acid-base parameters of probe liquids. To determine the electron-donor and electron-acceptor parameters in surface tensions for monopolar and bipolar liquids, van Oss *et al.* [22–27] assumed $\gamma^{-} = \gamma^{+} = 25.5$ mJ m^{-2} for water as the standard bipolar liquid. As mentioned above, also a negative value of square root is obtained in some systems for electron-acceptor interactions [5, 35].

Lee [36], however, has very recently presented an interesting approach to the problem of the reference γ^{-} and γ^{+} parameters for water. Considering Taft and Kamlet's [37] solvatochronic parameters of "linear free energy relationship", or "linear solvation energy relationship" (LSER), which concern a solvation process, he has found for water that a more appropriate ratio of γ^{+}/γ^{-} is 1.8 instead of 1, as assumed by van Oss *et al.* [22–27]. This leads to new values of these parameters not only for water but also for all probe liquids used for contact angle measurements [1–3] or thin layer wicking technique [9–14]. Lee [36] has recalculated the literature data for many polymers, proteins and others and he found that the new acidic and basic parameters for probe liquids in general cause a decrease of the basic parameter γ^{-} and a slight increase of γ^{+} parameter of the solids. As the author stated, this finding does not solve the problem of determination of the interfacial free energy components, but it is a step to learn these parameters more closely.

Besides the problem of theoretical description of interfacial interactions, the experimental circumstances have to be taken into account. In an earlier paper [12] it was studied whether the thickness of porous layer of a solid (silica gel) affects the penetration rate of probe liquids, and in consequence the value of the determined components of surface free energy. Using commercial SiO_2 plates (Merck), the same values of components of silica gel surface free energy were obtained for a powdered layer even up to 2 mm in thickness. This is of a special importance, when the coating is made in the laboratory by water evaporation, and the obtained layer can differ a little in thickness in different places of the plate.

In this paper, for further testing of the thin layer wicking method, the effect of the kind of substrata, on which the porous layer of SiO_2 is deposited, on the determined magnitude of the surface free energy components was studied. For this purpose the commercial plates (Merck, applied in TLC) were used with a layer of silica gel deposited on a glass plate, aluminium or plastic sheet. Also, two kinds of chambers were used in this study: one was made in our laboratory and another was a typical commercial sandwich chamber used in TLC.

From the penetration rate of the selected probe liquids, using the theoretical models described in earlier papers [9–14], the components of SiO_2 surface free energy were calculated according to both approaches: geometric mean of dispersion and polar [20, 21] and Lifshitz-van der Waals acid-base interactions [22–27]. These two approaches were also used for calculation of the components of surface free energy of glass, aluminium and plastic substrata on which SiO_2 was deposited. In this case the components were determined from measured contact angles of diiodomethane, α-bromonaphthalene, water, formamide, glycerol and ethylene glycol.

For calculation of the values of surface free energy components using LWAB approach the surface tension components of probe liquids determined by van Oss *et al.* [22–27] and Lee [36] were used Moreover, it was also analyzed, whether the negligence of electron-acceptor and electron-donor interactions for diiodomethane and α-bromonaphthalene lead to significant differences in the calculated values of surface free energy components [22–27].

From the determined surface free energy components of glass, aluminium and plastic substrata the total surface free energy was calculated and then compared with the data calculated from the equation of state [28, 29].

2. Experimental procedure

2.1. Liquids

All liquids used were pure for analysis or chromatography. Water was obtained from Millipore reverse-osmosis filtration unit. Table I contains the literature values of the surface tension and its components of the probe liquids [25, 27, 36, 38–40].

2.2. The thin layer wicking experiments

The thin layer wicking experiments were conducted in the same way as described elsewhere [9–14]. As a model solid silica gel 60 deposited on the plates for thin layer chromatography (TLC) was used (Merck):

– TLC glass plates silica gel 60 (layer thickness 0.25 mm),

– TLC aluminium sheets silica gel 60 (layer thickness 0.2 mm),

– TLC plastic sheets silica gel 60 (layer thickness 0.2 mm).

TABLE I The surface tension components of probe liquids in mN m^{-1} at 20 °C

Liquid	γ_l	γ_l^d	γ_l^p	Ref.	γ_l	γ_l^{LW}	γ_l^+	γ_l^-	Ref.	γ_l	γ_l^{LW}	γ_l^+	γ_l^-	Ref.
Nonane	22.91	22.91	0	[38]	22.91	22.91	0	0		22.91	22.91	0	0	
Decane	23.9	23.9	0	[38]	23.9	23.9	0	0		23.9	23.9	0	0	
Diiodomethane (D)	50.8	50.4	0.4	[40]	50.8	50.8	≈0	0	[27]	50.8	50.8	0	0	[36]
						50.8	0.7	0	[25]					
α-Bromonaphthalene (B)	44.6	43.7	0.9	[40]	44.4	44.4	≈0	≈0	[27]	44.4	43.5	0	0	[36]
					44.4	43.6	0.4	0.4	[25]					
Water (W)	72.8	21.8	51.0	[39, 40]	72.8	21.8	25.5	25.5	[27]	72.8	21.8	34.2	19	[36]
Formamide (F)	58.4	31.4	27.0	[40]	58.0	39.0	2.28	39.6	[27]	58	39	3.1	29.1	[36]
Glycerol (G)	63.3	33.6	29.7	[40]	64.0	34.0	3.92	57.4	[27]	64	34	5.3	42.5	[36]
Ethylene glycol (E)	48.2	31.5	16.7	[40]	48.0	29.0	1.92	47.0	[27]	48	29	2.6	34.8	[36]

All plates were without fluorescent indicator. The plates for thin layer wicking experiments, 10 × 2.5 cm in size, were cut off from a large silica plate.

The penetration of the liquids was conducted in two different chambers:

– The chamber made of aluminium, in which the top wall was a glass plate [9–11]. The chamber was placed at 12° angle. During measurement one end of the plate (about 3 mm) was placed in a small Petri dish into which a little probe liquid was poured.

– The commercial sandwich chamber made by Chromdes (Lublin, Poland) for thin layer chromatography. In this case the construction of the chamber allows the liquid to penetrate the layer deposited on the substratum in horizontal position. The front of the penetrating liquid was observed through the substratum.

In the case of glass plates and aluminium sheets measurements were made using the first chamber, whereas in that of plastic sheets the chamber of the second type was applied. Prior to wicking experiments the plates were heated at the following temperatures:

– glass plates and aluminium sheets were heated for 2 h at 130°C,

– plastic sheets were dried in a vacuum for 2 h at 80°C.

Dried plates were stored in a desiccator with a molecular sieve, or kept in closed vessels with saturated vapor of the liquid studied. The time of the silica gel contact with the liquid vapor was 24 h.

Wicking experiments for decane, diiodomethane, α-bromonaphthalene, water, formamide were made at 20 ± 0.1°C for bare (b) and precontacted (p) surface of silica gel using all kinds of the plates.

2.3. Calculation of surface free energy components from penetration rate

A general form of Washburn equation allows determination of surface free energy components of a solid from the penetration rate of probe liquids for bare and precontacted surface [9–14]:

$$x^2 = \frac{Rt}{2\eta}\Delta G \tag{1}$$

where x is the distance at which the liquid displaces in time t, η is the liquid viscosity, R is the effective radius of interparticle capillaries and ΔG is the change of the specific free energy accompanying liquid penetration into the porous layer.

For completely wetting liquids (no contact angle) the driving force in case of bare solid surface is equal to the work of spreading (the difference between the work of adhesion and cohesion of the liquid), $\Delta G_b = W_S = \gamma_s - \gamma_l - \gamma_{sl} = W_A - W_C$:

$$\Delta G_b = \left(\gamma_s^{LW}\gamma_l^{LW}\right) - 2\gamma_l \tag{2}$$

where $\gamma_l^{LW} = \gamma_l$ for n-alkanes.

For liquids, which form defined contact angle on a flat surface of the studied solid, we consider that the liquid penetrate the interparticle pores in the thin porous layer at a dynamic advancing (in the case of the bare surface) and the dynamic receding (precontected with the liquid vapor surface) angles (not contact angles appropriate for Young equation) [9–14]. The corresponding free energy change is related to the difference between the specific change of energy calculated from Equation 1 for bare, ΔG_b, and precontacted, ΔG_p, which is equal to, $\Delta G_b - \Delta G_p = W_A - W_C$.

Thus for the model of acid-base interactions at solid-liquid interface (LWAB) [9–14] the folowing relationship can be given:

$$\begin{aligned}\Delta G_b - \Delta G_p = W_A - W_C = 2\left(\gamma_s^{LW}\gamma_l^{LW}\right)^{1/2}\\ + 2\left(\gamma_s^{+}\gamma_l^{-}\right)^{1/2} + 2\left(\gamma_s^{-}\gamma_l^{+}\right)^{1/2} - 2\gamma_l.\end{aligned} \tag{3}$$

In the case of apolar liquids, in Equation 3 the terms concerning acid-base interactions are reduced. In the approach (GM) based on the geometric mean from apolar and polar interactions it is:

$$\Delta G_b - \Delta G_p = 2\left(\gamma_s^{d}\gamma_l^{d}\right)^{1/2} + 2\left(\gamma_s^{p}\gamma_l^{p}\right)^{1/2} - 2\gamma_l \tag{4}$$

2.4. Contact angle measurements

Contact angles measurements were performed at 20 ± 0.1°C by the sessile drop method using a microscope-goniometer system at 25× magnification. A 2 μl liquid drop (diiodomethane, α-bromonaphthalene, water, formamide, glycerol, ethylene glycol) was settled by microsyringe and the contact angle was read out both from the left and right side. Measurements of advancing contact angles were made on glass plates, aluminium and plastic sheets, from which the silica gel layer had been removed. Thus prepared plates were washed in double distilled water with ultrasounds, then dried: the glass plates and aluminium sheets at 130°C for 2 h, and the plastic sheets in vacuum at 80°C for 2 h. Prior to the contact angle measurements the plates were stored in a desiccator with a molecular sieve.

2.5. Calculation of surface free energy and its components from contact angles

2.5.1. The Lifshitz-van der Waals acid-base approach – LWAB

Interfacial free energy (γ_{12}) of two contacting phases 1 and 2 is expressed by the equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^{\mathrm{LW}}\gamma_2^{\mathrm{LW}}\right)^{1/2} - 2\left(\gamma_1^{+}\gamma_2^{-}\right)^{1/2} - 2\left(\gamma_1^{-}\gamma_2^{+}\right)^{1/2} \qquad (5)$$

In the case of contact angle (θ) the work of adhesion is described by the following relationship:

$$(\cos\theta + 1)\gamma_1 = 2\left(\gamma_s^{\mathrm{LW}}\gamma_1^{\mathrm{LW}}\right)^{1/2} + 2\left(\gamma_s^{+}\gamma_1^{-}\right)^{1/2} + 2\left(\gamma_s^{-}\gamma_1^{+}\right)^{1/2} \qquad (6)$$

This equation contains three unknown parameters. Measuring the contact angles of three liquids with known parameters: γ_1^{LW}, γ_1^{-}, γ_1^{+} the components of surface free energy can be determined. Using the approach of van Oss *et al.* [22–27] the total surface free energy of a solid or liquid can be divided into two parts:

$$\gamma = \gamma^{\mathrm{LW}} + \gamma^{\mathrm{AB}} \qquad (7)$$

2.5.2. The geometric mean of apolar and polar interaction approach – GM

In this case interfacial free energy is expressed by the following relationship:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\left(\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}\right)^{1/2} - 2\left(\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}\right)^{1/2} \qquad (8)$$

where γ^{p} involves dipole-dipole interactions, hydrogen bonding or both. Then, from Young equation W_{A} can be given:

$$(\cos\theta + 1)\gamma_1 = 2\left(\gamma_s^{\mathrm{d}}\gamma_1^{\mathrm{d}}\right)^{1/2} + 2\left(\gamma_s^{\mathrm{p}}\gamma_1^{\mathrm{p}}\right)^{1/2} \qquad (9)$$

In Equation 9 two parameters are unknown: γ_s^{d} and γ_s^{p}. They can be determined from two equations when contact angles for liquids are measured, for which γ_1^{d} and γ_1^{p} are known. In this approach the surface free energy is considered as a sum of the dispersion, γ^{d}, and the nondispersion, γ^{p}, components:

$$\gamma = \gamma^{\mathrm{d}} + \gamma^{\mathrm{p}} \qquad (10)$$

2.5.3. The equation of state approach – ES

The so-called equation of state for the interfacial free energy can be expressed [28, 29]:

$$\gamma_{12} = \frac{\left[(\gamma_1)^{1/2} - (\gamma_2)^{1/2}\right]^2}{1 - 0.015(\gamma_1\gamma_2)^{1/2}} \qquad (11)$$

On the basis of the contact angle measured for one liquid only the total surface free energy of solid, γ_s, can be calculated:

$$\gamma_s - \frac{\left[(\gamma_s)^{1/2} - (\gamma_l)^{1/2}\right]^2}{1 - 0.015(\gamma_s\gamma_l)^{1/2}} = \gamma_l\cos\theta \qquad (12)$$

It is usually assumed that for such systems for which $\theta > 0$ the film pressure of the liquid on the solid surface is equal to $\pi_e = 0$ [1–5, 28, 29].

3. Results and discussion

Before the determination of surface free energy components by using the thin layer wicking method it is necessary to find an effective radius of the interparticle pores formed in porous silica gel layer. This is possible when the surface free energy of a solid is depressed to the value corresponding to surface tension of a hydrocarbon, i.e. apolar liquid completely wetting the solid (no contact angle), e.g. due to the formation of adsorption film (by contacting the surface with saturated vapor of *n*-alkane). Then in Equation 1 ΔG is equal to $\Delta G_{\mathrm{p}} = \gamma_l$.

Fig. 1 shows the penetration rate for two alkanes: *n*-nonane and *n*-decane (mean values from at least 4–6 measurements) in porous silica gel layer on a glass plate for precontacted (curves 1p, 2p) and bare (curves 1b, 2b) surfaces. As mentioned in the "Experimental" section the penetration rate measurements were performed in two kinds of chambers. In the case of glass plates the

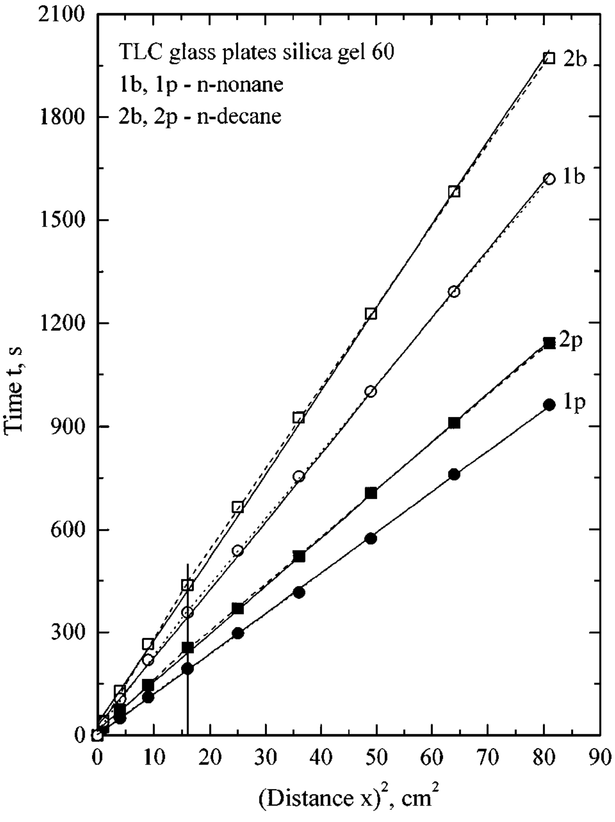

Figure 1 $x^2 = f(t)$ functions for *n*-nonane (curves 1) and *n*-decane (curves 2) wicking bare (b) and percontacted (p) surface of silica gel 60 deposited on glass plates. The penetration rate of *n*-alkanes was measured in the aluminium chamber.

TABLE II The effective radius (R) of the interparticle capillaries in the porous layer of silica gel 60 (layer thikness 0.25 mm)

Penetrated distance, cm	The effective radius R, $\times 10^{-5}$ cm		
	R_9	R_{10}	Av $\bar{R}$
0–4	4.141	4.831	4.486 ± 0.488
4–9	5.278	5.654	5.466 ± 0.266
0–9	5.266	5.465	5.366 ± 0.141

measurements were performed in a chamber made in our laboratory (aluminium chamber).

As it is seen in Fig. 1, two straight-line sections can be found, slightly differing in the slope: one from 0–4 cm, the other from 4–9 cm of the penetrated distances. Similar relationships, though difficult to interpret, were obtained in earlier studies [9–11]. Thus, it was interesting to find out how the changing sloping affected the calculated components of the surface free energy of silica gel. Using the results from Fig. 1 for precontacted surface, the effective radius was determined for three penetrations ranges, i.e. 0–4 cm, 4–9 cm and the whole penetration range, 0–9 cm, by the least squares method the linear equation were adjusted. The values of effective radii for two hydrocarbons (nonane and decane) with consideration of the particular sections are listed in Table II. For the first straight-line section somewhat smaller $\bar{R}_{0-4}$ values were obtained, while for the second section the $\bar{R}_{4-9}$ values are more suitable for the entire penetration range.

Applying all the calculated mean values of two alkanes, for the particular ranges: $\bar{R}_{0-4}$, $\bar{R}_{4-9}$, and the function $x^2 = f(t)$ for bare silica gel surface for these hydrocarbons, the value of Lifshitz-van der Waals component, γ_s^{LW}, was determined from Equation 2. It was assumed that the change of free energy accompaning n-alkane penetration is equal to the work of wetting by spreading [9–14]. The calculated values of the apolar component, γ_s^{LW}, of silica gel are given in Table III. As it can be seen, the values of this component are practically the same for all cases. Therefore, in further calculations of surface free energy components a mean radius ($\bar{R}_{0-9}$) was used. It was experimentally determined from penetration of alkanes on precontacted surface.

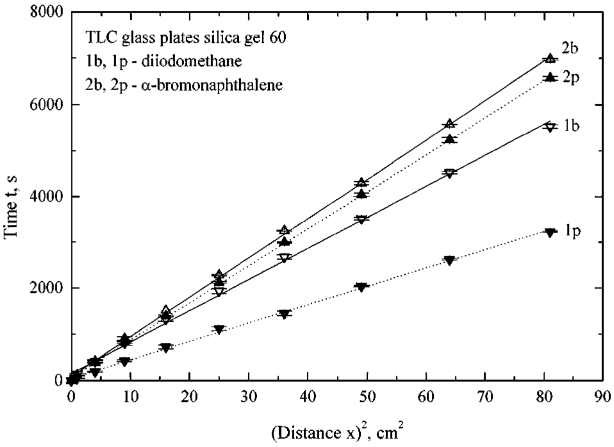

Figure 2 The same relationships as in Fig. 1 but for diiodomethane and α-bromonaphthalene.

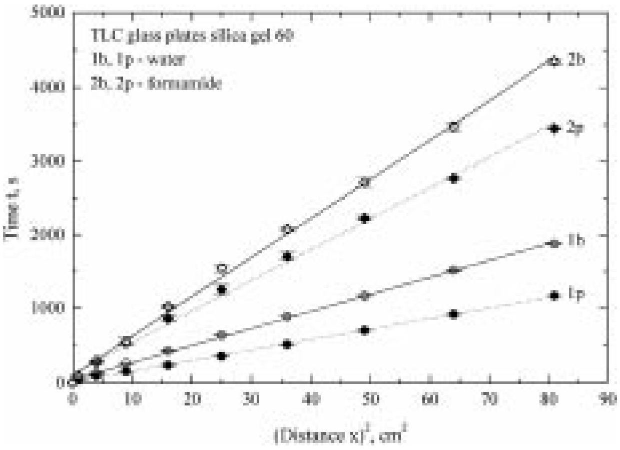

Figure 3 The same relationships as in Fig. 1 but for water and formamide.

Besides, two other liquids were used to determine this value, namely diiodomethane and α-bromonaphthalene. Van Oss *et al.* [26] have proposed to use these liquids for determination of Lifshitz-van der Waals component, assuming that they are apolar liquids, i.e. neglecting, small acid-base (acceptor-donor) interactions. The presence of iodine in diiodomethane molecule indicates that γ_l^+ should be greater than zero. An electronegative atom as well as and π electrons are present α-bromonaphthalene molecule, thus this liquid should demonstrate the weak electron-donor, γ_l^-, and electron-acceptor, γ_l^+, interactions. Therefore, in further considerations these liquids will be treated either as apolar, or as weakly polar.

Fig. 2 shows the penetration rate of two apolar liquids: diiodomethane and α-bromonaphthalene while in Fig. 3 for two polar ones: water and formamide on bare

TABLE III Surface free energy components: apolar, Lifshitz-ven Waals (γ_s^{LW}), acid-base (γ_s^{AB}): electron-acceptor (γ_s^+) and electron-donor (γ_s^-), and total surface free energy (γ_s) of silica gel (in mJ m^{-2}) determined from wicking experiments for TLC glass plates silica gel 60 (surface tension components of probe liquids taken from literature [27, 36, 38])

	SiO$_2$ 60, glass plates													
	γ_s^{LW}					$\bar{\gamma}_s^{LW}$	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
R	nonane C$_9$	decane C$_{10}$	Av C$_{9,10}$	D	B	Av. B, D, C$_{9,10}$		from W and F [27]				from W and F [36]		
$\bar{R}_{0-4}$	39.0	40.9	39.9	39.9	43.0	40.9 ± 1.8	1.2	38.0	13.5	54.4	1.6	28.3	13.5	54.4
$\bar{R}_{4-9}$	38.7	40.6	39.6	42.5	43.6	41.9 ± 2.1	0.4	51.3	9.1	51	0.5	38.3	8.8	50.7
$\bar{R}_{0-9}$	38.3	40.1	39.3	40.3	43.4	41.0 ± 2.1	0.5	45.6	9.5	50.5	0.7	34.1	9.8	50.8

and pre-contacted surface. From these relationships ΔG_b and ΔG_p from Equation 1 and the Lifshitz-van der Waals component from Equation 3 were calculated. Then from simultaneous of solution of two Equations 3: electron-acceptor, γ_s^+, and electron-donor, γ_s^-, parameters of silica gel surface free energy were determined using the mean value of $\bar{\gamma}_s^{LW}$ for two hydrocarbons, diiodomethane and α-bromonaphthalene. From the value $\bar{\gamma}_s^{LW}$ and the data in Fig. 3 the parameters γ_s^+ and γ_s^- were calculated for the particular penetration sections, basing on the values of surface tension components of water and formamide from paper of van Oss [27] and on the new data from Lee's paper [36]. The obtained values are listed in Table III.

As it appears from Table III, that in the case of diiodomethane and α-bromonaphthalene a slightly higher γ_s^{LW} value was obtained than for alkanes. The values of γ_s^-, from the first straight line section (0–4 cm) are lower than for the second one (4–9 cm) as well as from the data of van Oss [27] and lee [36]. When the whole penetration range (0–9 cm) is taken into consideration [27], $\gamma_s^- = 45.6$ mJ m^{-2}, a good agreement is obtained with γ_s^- of silica gel [11].

Similar experiments and calculations (for the whole penetration range 0–9 cm) were performed for silica gel samples which porous layer was deposited on aluminium and plastic sheets. From the penetration rate of nonane, decane, diiodomethane and α-bromonaphthalene (not reported here) the values of γ_s^{LW} were calculated. Then the electron-acceptor and electron-donor interactions of surface free energy of silica gel 60 were determined from the penetration of water and formamide and calculated values of Lifshitz-van der Waals component (from van Oss [27] and Lee [36]). Table IV presents these values as well as mean ones with standard deviation. For full illustration of interfacial interactions those of acid-base interaction, γ_s^{AB}, and total surface free energy, γ_s, are also listed. As it can be seen, very close values of surface free energy components of silica gel were obtained (maximum standard deviation is 2.5 mJ m^{-2}).

Comparing the results presented in Table III and IV it can be found, that a perfect agreement was obtained for all the surface free energy components calculated for the values of surface tension from paper of van Oss [27]. The mean values of the components of silica gel (for three kinds of substrata) are equal to $\bar{\gamma}_s^{LW} = 40.7 \pm 0.5$ mJ m^{-2}, $\bar{\gamma}_s^- = 44.6 \pm 1.1$ mJ m^{-2}, $\bar{\gamma}_s^+ = 0.7 \pm 0.2$ mJ m^{-2}, $\bar{\gamma}_s^{AB} = 11.4 \pm 1.6$ mJ m^{-2}, and the total surface free energy $\bar{\gamma}_s = 52.0 \pm 1.5$ mJ m^{-2}. As it is seen, the substrata on which the porous layer was deposited as well as its thickness (0.25 mm on glass plates, 0.2 mm on aluminium and plastic sheets) did not practically affect the determined value of components of surface free energy. The different measurement chambers used for penetration rate experiments did not influence the determined values.

The values of surface free energy components of silica gel determined on three different substrata obtained with the help of the new data of surface tension components for water and formamide [36], were in very good agreement. A decrease of the γ_s^- value by about 25% (from 44.6 to 33.3 ± 0.9 mJ m^{-2}) and slight increase in γ_s^+ (from 0.7 to 1.0 ± 0.3 mJ m^{-2}) were found, whilst γ_s^{AB} and γ_s practically remained unchanged (Table III and IV).

Alkanes used for determination of Lifshitz-van der Waals component provided a little lower γ_s^{LW} value was than that obtained for diiodomethane and α-bromonaphthalene. As mentioned earlier, van Oss [27] suggested to neglect acceptor-donor interactions of the latter liquids at solid-liquid interface, i.e. $\gamma_l^- = \gamma_l^+ = 0$.

TABLE IV Surface free energy components: apolar, Lifsbitz-van der Waals (γ_s^{LW}), acid-base (γ_s^{AB}): electron-acceptor (γ_s^+) and electron-donor (γ_s^-), and total surface free energy (γ_s) of silica gel (in mJ m^{-2}) determined from wicking experiments for TLC aluminium and plastic sheets silica gel 60

SiO$_2$									
Aluminium sheets					Plastic sheets				
γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
van Oss [27]									
37.8a)	1.5	43.2	16.1	53.9	38.1a)	1.1	44.4	14.0	52.1
38.8b)	1.3	43.3	15.0	53.8	38.8b)	1.1	44.4	14.0	52.8
38.3c)	1.4	43.3	15.3	53.6	38.5c)	1.1	44.4	14.0	52.5
42.4d)	0.7	43.7	11.1	53.5	39.4d)	0.9	44.5	12.7	52.1
42.1e)	0.7	43.6	11.0	53.1	42.4e)	0.5	44.8	9.5	51.9
40.9f)	0.9	43.5	12.5	53.4	40.1f)	0.8	44.6	12.1	52.2
±2.3	±0.4	±0.2	±2.5	±0.3	±2.0	±0.3	±0.2	±2.3	±0.3
Lee [36]									
40.9f)	1.3	32.4	12.6	53.5	40.1f)	1.1	33.3	11.7	51.8
±2.3	±0.5	±0.2	±2.2	±0.1	±2.0	±0.4	±0.1	±2.5	±0.4

γ_s^{LW} determined from:
a) *n*-nonane.
b) *n*-decane.
c) average from *n*-nonane and *n*-decane.
d) diiodomethane.
e) α-bromonaphthalene.
f) average from (c-e).

TABLE V Surface free energy components: apolar, Lifshitz-van der Waals (γ_s^{LW}), acid-base (γ_s^{AB}): electron-acceptor (γ_s^+) and electron-donor (γ_s^-), and total surface free energy (γ_s) of silica gel (in mJ m^{-2}) determined from wicking experiments for TLC glass plates, aluminium and plastic sheets silica gel 60; diiodomethane and α-bromonaphthalene as weakly polar liquids [25]

	SiO_2 60														
	Glass plates					Aluminium sheets					Plastic sheets				
Liquids	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^-	γ_s^-	γ_s^{AB}	γ_s
DWF	30.9	2.5	44.5	21.1	52.0	32.8	2.7	42.8	21.5	54.3	30.1	2.7	43.6	21.7	51.8
BWF	34.7	1.5	44.9	16.4	51.1	32.9	2.8	42.8	21.9	54.8	33.6	2.8	43.7	22.1	55.7
Av.	32.8	2.0	44.7	18.8	51.6	32.9	2.7	42.8	21.7	54.6	31.9	2.8	43.7	21.9	53.8
	±2.7	±0.7	±0.3	±3.3	±0.6	±0.1	±0.1	±0	±0.3	±0.4	±2.5	±0.1	±0.1	±0.3	±2.8

However, in further investigations these interactions were taken into account, and from the penetration rate the surface free energy components of silica gel were determined for two sets of three liquids: DWF (diiodomethane, water and formamide) and BWF (α-bromonaphthalene, water and formamide). An analysis carried out for five liquids commonly used for contact angle measurements [4], i.e. water, glycerol, formamide, diiodomethane and bromoform showed that among the ten possible combinations the sets of three liquids: water-glycerol-diiodomethane, water-formamide-diiodomethane, water-glycerol-bromoform, water-formamide-bromoform were the best for determination of γ_s^{LW} and γ_s^{AB} of surface free energy of solids. In this case the error in contact angle measurements for these liquids caused the smallest error in calculations of these values. Besides the liquids mentioned van Oss *et al.* [26] used also α-bromonaphthalene and ethylene glycol. It results from this that for calculation of surface free energy components of solids by the method of van Oss *et al.* [22–27] the most suitable set of liquids which consists of an apolar liquid (in fact a weakly polar) with a high surface tension, and two polar liquids. They are different considerably in the values of γ_l^{LW}, γ_l^- and γ_l^+.

Table V presents the values of surface free energy components of silica gel determined, using $\gamma_l^+ = 0.7$ mN m^{-1} for diiodomethane and $\gamma_l^- = \gamma_l^+ = 0.4$ mN m^{-1} for α-bromonaphthalene [25]. The mean values of the particular components of silica gel are (for three kinds of plates) $\bar{\gamma}_s^{LW} = 32.5 \pm 0.6$; $\bar{\gamma}_s^+ = 0.5 \pm 0.4$; $\bar{\gamma}_s^- = 43.7 \pm 1.0$; $\bar{\gamma}_s^{AB} = 20.8 \pm 1.7$ and $\bar{\gamma}_s = 53.3 \pm 1.6$ mJ m^{-2}. As it is seen, the introduction of acid-base parameters in the surface tension of these two liquids leads to considerable differences in the values of surface free energy components (Table III–V). The values of γ_s^{LW} decreases from 40.7 to 32.5 mJ m^{-2}, which gives 25.2% difference of this component value, γ_s^+ increases from 0.7 to 2.5 mJ m^{-2}, while γ_s^- and γ_s do not practically change (44.7 to 43.7 and 52.0 to 53.3 mJ m^{-2}, respectively).

Thus, the assumption that diiodomethane or α-bromonaphthalene interacts with the adjacent phase only by Lifshitz-van der Waals forces results in considerable differences in values of apolar γ_s^{LW}, γ_s^+ and γ_s^{AB}, and thereby in predicting free solid-liquid interfacial energy γ_{sl}.

The value of γ_s^- is much higher for the studied silica gel than γ_s^+ i.e. the basic character of the surface predominates. The same tendency in values of surface free energy components can be found for many studied polar solids [5, 9–13, 36]. The determined component values seem to depend on the method used. For example, the values of silica gel components determined from adsorption isotherms by gas chromatography are electron-acceptor, $\gamma_s^+ = 45.1$ mJ m^{-2} and electron-donor $\gamma_s^- = 6.12$ mJ m^{-2}, thus the acid character of the surface predominates [8]. It is obvious because the silica gel surface is conditioned with dry hydrogen in a chromatographic column before the measurements. However, during the measurements, e.g. of contact angles [5] or thin layer wicking [9–13] the studied surface contacts with the air and the water vapor from the atmosphere.

As it results from the studies of Jańczuk and Zdziennicka [1], the changes in wettability of quartz by water and organic liquids as a function of air humidity and the time of quartz contact with water, are the result of the changes in surface free energy components due to adsorption of water molecules on the solid surface and the suitable structure of the formed film. A strong orientation of water molecules occurs at the expense of the decreased surface free energy of quartz, which in consequence causes a considerable decrease in quartz surface interactions (polar component).

The properties of silica gel surface depend on the geometric structure and chemical character of the surface [41]. After removing the physically adsorbed water (heating in vacuum at 200°C) hydroxyl groups (silanols – 4.6 OH nm^{-2}) remain on the surface. They are strong adsorption sites owing to the specific interactions with the adsorbate molecules (the formation of hydrogen bonding) and siloxane bridges considered as hydrophobic sites [41].

From the determined surface free energy components: γ_s^{LW}, γ_s^+ and γ_s^- of the studied silica gel it can be concluded that water molecules are adsorbed with the hydrogen atoms oriented towards the hydroxyl group (the acid end in Lewis's theory) due to the fact that the silica surface becomes electron-donor (basic). Such a model of hydrogen bond formation is more likely, and it has been confirmed by Grivtsov [42] with the help of numerical modeling by molecular dynamics.

There should be taken into consideration also the possibility of dissociation of surface hydroxyl groups in the presence of water and the resulting formation of a negative charge on the surface. In this situation the water dipoles are oriented by the positively charged part

TABLE VI Surface free energy components of silica gel (in mJ m^{-2}): dispersion (γ_s^d) and polar (γ_s^p) determined from wicking experiments for TLC glass plates, aluminium and plastic sheets (surface tension components of probe liquids taken from Ref. [40])

	SiO_2 60								
	Glass plates			Aluminium sheets			Plastic sheets		
Liquids	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
DW	34.5	31.6	66.1	36.5	31.0	67.5	33.6	33.4	67.0
DF	36.1	17.0	53.1	37.8	17.6	55.4	34.9	17.1	52.0
BW	35.2	31.2	66.4	33.8	32.7	66.5	34.1	32.0	66.1
BF	35.9	19.2	55.1	36.6	14.9	51.5	36.4	17.6	54.0
Av	35.4 ±0.7	24.8 ±7.7	60.2 ±7.1	36.2 ±1.7	24.0 ±9.1	60.2 ±8.0	34.8 ±1.2	25.0 ±8.9	60.0 ±7.9

TABLE VII Contact angles, and their standard deviations (degrees) for the liquids measured on the glass platess, aluminium and plastic sheets

Type of plates	θ_D	θ_B	θ_W	θ_F	θ_G	θ_E
Glass plates	43.0 ± 2.7	26.0 ± 1.5	33.7 ± 2.6	25.0 ± 2.9	29.9 ± 1.8	14.3 ± 1.5
Aluminium sheets	44.0 ± 2.2	33.8 ± 3.5	71.5 ± 3.7	66.3 ± 3.8	77.1 ± 2.4	65.3 ± 2.9
Plastic sheets	41.4 ± 2.0	25.5 ± 3.9	75.6 ± 2.4	51.6 ± 3.4	60.4 ± 3.3	43.9 ± 1.2

towards the silica surface, whereby the surface becomes electron-donor. It seems that water molecules adsorbed on silica gel essentially change the surface properties of this adsorbent.

From the literature data it appears that for many systems the values of surface free energy components calculated through the geometric mean of apolar and polar interactions [20, 21] and according to the model of Lifshitz-van der Waals and acid-base interactions [22–27] are practically the same [1–3]. To test this for the silica gel studied the components, γ_s^d, and γ_s^p, of the surface free energy of silica were also calculated from the results presented in Figs 1–3 and on the basis of γ_l, γ_l^d and γ_l^p values for probe liquids (Table I). The values of the dispersion and polar components of the gel determined from Equation 4 are shown in Table VI. From this table appears that, the mean values of $\bar{\gamma}_s^d = 35.5 \pm 0.7\,\mathrm{mJ\,m^{-2}}$ and $\bar{\gamma}_s^p = 24.6 \pm 0.5\,\mathrm{mJ\,m^{-2}}$ of silica gel on three kinds of plates do not differ significantly from that $\bar{\gamma}_s^{LW} = 32.5$ and $\bar{\gamma}_s^{AB} = 20.8$ mJ m^{-2}, when diiodomethane and α-bromonaphthalene are considered as weakly polar liquids (Table V). However, considerable differences occur when the above liquids are considered apolar ($\bar{\gamma}_s^{LW} = 40.7$ and $\bar{\gamma}_s^{AB} = 11.4\,\mathrm{mJ\,m^{-2}}$). The average value of the total surface free energy of silica gel calculated for these components is equal to 60.1 ± 0.1 (from GM) and it is higher than $53.3 \pm 1.6\,\mathrm{mJ\,m^{-2}}$ (LWAB).

As it has been stated above, although the silica gel layer was on different substrata (glass plate, aluminium and plastic sheets) the determined values of the particular components of SiO_2 surface free energy were practically the same. Nevertheless, the determination of the substratum surface free energy seemed interesting, therefore the contact angle were measured for six liquids: diiodomethane, α-bromonaphthalene, formamide, water, glycerol and ethylene glycol. The mean values of the contact angle are given in Table VII. The contact angles for diiodomethane, α-bromonaphthalene on all kinds of plates are very similar, while for polar liquids they are definitely larger on aluminium and plastic sheets. On the surface of glass plate the largest contact angle is formed for diiodomethane, and the smallest one for ethylene glycol. On aluminium sheets the contact angle values for water and glycerol are very close and comparable to water contact angle on plastic sheets. On plastic sheet the contact angle values of diiodomethane, α-bromonaphthalene, water and formamide are comparable with those for perspex [5].

Taking the contact angle values from Table VII one can calculate (Eqatuions 5 and 8) the components: Lifshitz-van der Waals and acid-base as well as dispersion and polar ones of surface free energy of the plates studied, assuming that the film pressure of the liquids is $\pi_e = 0$. The results are listed in Tables VIII and IX considering diiodomethane and α-bromonaphthalene either as apolar liquids (Table VIII) or as weakly polar (Table IX). Analyzing the values of γ_s^{LW}, γ_s^+ and γ_s^- components it can be found, that with DWF and BWF sets for glass the obtained values of the components are the closed to mean values also presented in Tables VIII and IX. In the case of aluminium and plastic sheets every set of the liquids gives similar results of the components. The mean values have a small standard deviation (to 0.8 mJ m^{-2}), while in the case of glass plates it is maximally 5.3 mJ m^{-2} for the electron-donor component.

When diiodomethane and α-bromonaphthalene are considered as apolar liquids the γ_s^{LW} value for aluminium sheet is $37.4 \pm 0.2\,\mathrm{mJ\,m^{-2}}$, whereas for glass and plastic sheet: $39.1 \pm 1.0\,\mathrm{mJ\,m^{-2}}$ and $39.6 \pm 0.7\,\mathrm{mJ\,m^{-2}}$, respectively. Although the apolar interaction of the plates studied are very similar, their acid-base interactions are essentially different. The γ_s^- value is $40.6 \pm 5.3\,\mathrm{mJ\,m^{-2}}$ for glass, $20.9 \pm 0.3\,\mathrm{mJ\,m^{-2}}$ for aluminium sheet and $6.3 \pm 0.7\,\mathrm{mJ\,m^{-2}}$ for plastic sheet (Table IX). Despite the fact that changes were observed in γ_s^-, γ_s^+ and γ_s^{AB} values of the plates on which porous silica gel layer was deposited, it had no influence on the value of the determined surface free energy components of the silica gel studied (Table III and IV).

TABLE VIII Surface free energy components and total surface free energy (in mJ m^{-2}) of glass plates, aluminium and plastic sheets determined from contact angles of the probe liquids (Table VII); diiodomethane and α-bromonaphthalene as apolar liquids [27]

	Glass plates					Aluminium sheets					Plastic sheets				
Liquids	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
DWF	38.1	1.3	40.5	14.5	52.6	37.5	0.5	20.6	6.4	43.9	38.9	0.4	6.6	3.2	42.1
DWG	38.1	2.5	34.9	18.7	56.8	37.5	0.6	20.9	7.1	44.6	38.9	0.8	5.5	4.2	43.1
DWE	38.1	0.4	46.7	8.6	46.7	37.5	0.6	21.2	7.1	44.6	38.9	0.3	7.0	2.9	41.8
BWF	40.0	1.0	40.7	12.8	52.8	37.2	0.5	20.6	6.4	43.6	40.2	0.3	6.6	2.8	43.0
BWG	40.0	2.0	34.5	16.6	56.6	37.2	0.5	21.0	6.5	43.7	40.2	0.7	5.4	3.9	44.1
BWE	40.0	0.3	46.4	7.5	47.5	37.2	0.6	21.3	7.1	44.3	40.2	0.3	6.9	2.9	43.1
Av.[a)]	39.1	1.3	40.6	13.1	52.2	37.4	0.55	20.9	6.8	44.1	39.6	0.5	6.3	33.3	42.9
	±1.0	±0.9	±5.3	±4.4	±4.3	±0.2	±0.05	±0.3	±0.4	±0.4	±0.7	±0.2	±0.7	±0.6	±0.8
Av.[b)]	39.1	1.7	30.3	13.4	52.5	37.4	0.75	15.7	6.9	44.2	39.6	0.7	4.7	3.4	42.9
	±1.0	±1.2	±3.9	±4.3	±4.3	±0.2	±0.05	±0.2	±0.3	±0.4	±0.7	±0.3	±0.6	±0.5	±0.7

a) Average values calculated for surface tension components of probe liquids from van Oss [27].
b) Average values calculated for surface tension components of probe liquids from Lee [36].

TABLE IX Surface free energy components and total surface free energy (in mJ m^{-2}) of glass plates, aluminium and plastic sheets determined from contact angles of the probe liquids (Table VII); diiodomethane and α-bromonaphthalene as weakly polar liquids [25]

	Glass plates					Aluminium sheets					Plastic sheets				
Liquids	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s	γ_s^{LW}	γ_s^+	γ_s^-	γ_s^{AB}	γ_s
DWF	29.5	3.6	39.7	23.9	53.4	31.4	0.03	20.2	1.6	33.0	35.3	0.9	6.5	4.8	40.1
DWG	29.8	4.4	36.7	25.4	55.2	31.1	0.1	22.0	3.0	34.1	35.5	1.2	5.7	5.2	43.2
DWE	28.65	1.6	48.7	17.7	46.3	31.1	0.1	22.2	3.0	34.1	35.0	0.7	7.3	4.5	41.7
BWF	31.5	2.9	39.9	21.5	53.0	33.1	0.1	20.3	2.8	35.9	36.9	0.7	6.5	4.3	40.3
BWG	31.5	4.0	36.3	24.1	55.6	33.1	0.2	21.6	4.2	37.3	36.9	1.0	5.6	4.7	42.8
BWE	31.5	1.2	48.1	15.2	46.7	33.1	0.3	21.9	4.2	37.3	36.9	0.5	7.1	3.8	43.3
Av.	30.4	3.0	41.6	21.3	51.7	32.1	0.1	21.4	3.1	35.3	36.1	0.8	6.5	4.6	42.1
	±1.3	±1.3	±5.5	±4.0	±4.2	±1.0	±0.1	±0.9	±1.0	±1.0	±0.9	±0.3	±0.7	±0.5	±1.1

The values of the surface free energy and its components for the tested substrata, calculated with the help of the new data of surface tension component for water and formamide, are presented in Table VIII [36]. In this case the electron-donor parameter for the substrata was observed to decrease, and the electron-acceptor parameter to increase a little for the glass and plastic sheets, respectively. Both the values of acid-base interactions and the total surface free energy did not change.

If donor-acceptor interactions of diiodomethane and α-bromonaphthalene are taken into consideration the γ_s^{LW} values calculated for all kinds of plates are smaller. At the same time this causes an increase in electron-acceptor interactions. The electron-donor component, as in the case of the silica gel studied, practically remains unchanged.

Also the values of dispersion γ_s^d and polar γ_s^p components were calculated by using the geometric mean of dispersion and polar interactions [20, 21]. Calculations of γ_s^d and γ_s^p from Equation 9 were made for the following liquids pairs: DW, DF, DG, DE, BW, BF, BG and BE of which one was an apolar and the other polar liquid. The results are given in Table X. The calculated values of the dispersion component for all kinds of plates are similar, which is characterized by a small standard deviation. The values of the polar component are different for various liquid sets. For glass plates the γ_s^p value determined from the set of liquids: DG, DF, BG and BF is practically the same as the mean one, i.e. 21.4 mJ m^{-2}, while a considerable discrepancy of that from the set of liquids DW, DE, BW and BE occurs. Considerable differences in the value of this component are also found

TABLE X Components: dispersion (γ_s^d) and polar (γ_s^p) and total surface free energy (γ_s) of glass plates, aluminium and plastic sheets determined from contact angles (Table VII) of the used liquids, in mJ m^{-2} [40]

	Glass plates			Aluminium sheets			Plastic sheets		
Liquids	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s	γ_s^d	γ_s^p	γ_s
DW	32.4	31.6	64.0	34.8	8.2	43.0	36.6	5.8	42.4
DF	33.6	19.9	53.5	36.4	1.9	38.5	36.4	6.8	43.2
DG	33.4	22.1	55.5	37.2	0.4	37.6	36.7	5.0	41.7
DE	34.6	12.5	47.1	37.9	≈0	37.9	37.2	3.1	40.3
BW	32.0	31.7	63.7	33.4	8.6	42.0	37.1	5.7	42.8
BF	33.9	19.7	53.6	35.5	2.1	37.6	36.7	6.6	43.3
BG	33.4	22.0	55.4	36.8	0.4	37.2	37.3	4.8	42.1
BE	35.3	12.0	47.3	37.9	≈0	37.9	38.2	2.8	41.0
Av.	33.6	21.4	55.0	36.2	2.7	38.9	37.0	5.4	42.1
	±1.1	±7.4	±6.4	±1.6	±3.6	±2.2	±0.6	±1.5	±1.1

TABLE XI Surface free energy of glass plates, aluminium and plastic sheets calculated according to the equation of state from contact angles of the used liquids (Table VII)

	γ_s (mJ m^{-2})						
Type of plates	(D)	(B)	(W)	(F)	(G)	(E)	Average
Glass	39.3	40.4	65.6	53.2	57.5	74.5	55.1 ± 13.9
Aluminium	38.9	37.6	46.2	33.3	31.7	23.7	35.7 ± 6.7
Plastic	40.1	40.3	42.5	41.3	42.0	36.6	40.5 ± 2.1

for aluminium sheet, whereas for plastic sheet the values are approximate. These results also indicate which pairs of the liquids are suitable for determinations of the components.

For the last ten years the approach of van Oss *et al.* [22–27, 36] has mostly been used for description of interfacial interactions, and often for comparison the values of Owens and Wendt method [20] and Neumann's equation of state [28, 29] were also calculated. One of the most important conclusions resulting from this analysis is finding these approaches useful, in such process as adhesion, adsorption, wettability which depend on the surface free energy interactions [5, 15]. To compare three approaches the total surface free energy of the studied substrata was calculated from the determined components (Table VIII–X) as well as calculated from Neumann's equation of state (Equation 12) [28, 29] using the measured contact angles (Table VII). This calculated values are presented in Table XI. As it appears from the table the biggest standard deviation was obtained for glass plates ($\gamma_s = 55.1 \pm 13.9\,\mathrm{mJ\,m^{-2}}$) and the smallest for plastic sheets ($\gamma_s = 40.5 \pm 2.1\,\mathrm{mJ\,m^{-2}}$). The free energy of glass varies from 39,3 (diiodomethane) to 74.5 mJ m^{-2} (ethylene glycol). These values clearly show that "equation of state approach" is wrong. It is an experimental artifact that contact angle of diiodomethane on the glass plate was $43 \pm 2.7°$ (Table VII), and even if the total surface free energy of glass is 55 mJ m^{-2}, these is no contradiction. It is only a proof that the surface free energy can be really spitted into different interactions, and if diiodomethane interacts only by the dispersion (Lifshitz-van der Waals) forces, it amounts $32.8 \pm 2{,}7$ mJ m^{-2} (Table V).

From Table XII it can be found that applying the three approaches to describing interfacial interactions (LWAB, GM and ES) similar values of surface free energy are obtained, however, with different accuracy. The agreement among the γ_s values obtained by different methods does not mean that the three approaches are useful in the same way for the surface free energy determinations. A measure of the usefulness of a given approach can be found examining, for example, the solid-liquid interfacial interactions and the work of liquid adhesion to the solid surface [3].

4. Conclusions

From the investigations carried out it can be stated:

1. Using two models for description of interfacial free energy: acid-base and geometric mean approach, almost identical results of γ_s^{LW} and γ_s^{d} as well as γ_s^{AB} and γ_s^{p} were obtained both for the studied silica gel and plates used as substratum for porous silica layer.
2. The above agreement between the component values is obtained when electron-acceptor and electron-donor interactions for diiodomethane and α-bromonaphthalene taken into consideration.
3. Using the new values of the surface tension components for water and formamide was obtained a decrease in the value of electron-donor interactions and an increase of electron-acceptor interactions which, however are still low, whilst γ_s^{AB} and γ_s did not undergo any changes.
4. Neglecting electron-donor parameters in the surface tension of diiodomethane and α-bromonaphthalene causes considerable differences in the values of determined surface free energy components of silica gel (thin layer wicking method) and glass plates, aluminium and plastic sheets (contact angle measurements).
5. On the basis of three thermodynamic approaches (LWAB, GM and ES) comparable values of total surface free energy of the studied substrata were obtained, however, the best agreement have occurred for plastic sheets where acid-base interactions are smallest.
6. The thin laye wicking method is very useful for determination of surface free energy components of solids when it is difficult to measure contact angles. The kind of the chamber used for penetration rate measurement of a liquid, the thickness of the deposited layer as well as the kind of the substratum on which it has been deposited do not affect the value of the determined surface free energy components.

TABLE XII Total surface free energy of glass plates, aluminium and plastic sheets calculated using different thermodynamic approaches (from contact angles of the used liquids - Table VII)

	γ_s (mJ m^{-2})				
	LWAB				
	from Table 8		from Table 9		
Type of plates	[27]	[34]	[25]	GM	ES
Glass	52.2 ± 4.3	52.5 ± 4.3	51.7 ± 4.2	55.0 ± 6.4	55.1 ± 13.9
Aluminium	44.1 ± 0.4	44.2 ± 0.4	35.3 ± 1.8	38.9 ± 2.2	35.7 ± 6.7
Plastic	42.8 ± 0.8	42.9 ± 0.9	40.6 ± 0.8	42.1 ± 1.1	40.5 ± 2.1

LWAB - the Lifshitz-van der Waals acid-base approach.
GM - the geometric approach.
ES - the equation of state.

7. In the case of strongly polar solid, e.g. silica gel, the presence of adsorbed and oriented water molecules and electrostatic interactions cannot be ignored because they essentially effect surface free energy.

8. It seems that the approach taking into account quantitatively electron-donor and electron-acceptor interactions (hydrogen bonding) allows a better explanation of the phenomena occurring at interfaces, e.g. stability of the colloid system, enrichment of raw mineral materials, etc.

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