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Wettability of Coal Surface and its Surface Free Energy Components

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Contact angles were measured for various coal ranks — water drop — *n*-hexane, *n*-dodecane and *cis*-decalin systems. Using the results obtained the values of the dispersion and nondispersion components of the surface free energy of Polish coal of various ranks, from 31.1 to 35, were calculated. These values (γ_s^d and γ_s^p) were compared with those calculated on the basis of measurements of contact angles conducted earlier for various coal ranks — air bubble or hydrocarbons drop — water systems. The results obtained allowed us to conclude that, firstly, the surface free energy of coals results from both the dispersion and nondispersion intermolecular interactions and, secondly, that dispersion components of this energy depend on the coal ranks. The value of nondispersion components of the surface free energy does not depend on the coal ranks and should not exceed 10 mJ/m^2.

It was also found that taking into account the values of dispersion components of the studied coals surface free energy we can classify them into three groups: 1) coal rank 31, 2) coal rank 32 and 3) coal rank 33, 34 and 35.

INTRODUCTION

The wettability phenomenon of solids of which contact angle is a visible measure, plays an important role both in every day life and in many industrial branches.[1,2] Among them beneficiation of minerals and ores by the froth flotation method is based mostly on different wettabilities of the surface of useful and waste minerals.[3,4]

Froth flotation is also used to enrich coal slime.[4] It is possible to learn the mechanism of this process and its management when the surface properties of coal are known. Wettability is closely connected with these properties. Therefore, many attempts are made to determine the coal surface free energy as well as its changes under the influence of many different flotation reagents[5-9], on the basis of contact angle measurements[5-7,9] or on the basis of adsorption of nonpolar and polar liquids on coal surface.[8]

Aplan *et al.*[5,6] measured the contact angles in the systems: various coal ranks — liquids whose values of surface tension are different (nondispersion component of surface tension is not equal to zero) — air. Using Zisman's[10,11] method, they determined the critical surface tension of wetting of coals in the range from 43 to 50 mJ/m^2 (the average value being 45 mJ/m^2).

According to this finding, the critical surface tension of wetting does not practically depend on the coal rank, furthermore, measuring the contact angle of methylene iodide droplet on the surface of coal of various ranks[6], they calculated the dispersion component (γ_S^d) of the surface free energy of coals. These calculations were done assuming, firstly, that the methylene iodide surface tension results from dispersive intermolecular interaction. Secondly, that the adsorption of vapour methylene iodide molecules on the surface of coals behind the sessile liquid drop does not change the surface free energy of coals. They found that the γ_S^d value was identical with the average value of the critical surface tension of coal wetting (γ_c) and it did not depend on the coal rank. The identity between γ_S^d and γ_c may prove that the surface free energy of coal originates only from dispersive intermolecular interaction.

Studies conducted by Staszczuk *et al.*[8] on *n*-octane and *n*-propanol adsorption on the surface of coal from the Lublin Coal Basin showed that its surface free energy originated from dispersive and nondispersive intermolecular interactions. The dispersion component of the surface free energy of coal calculated from the adsorption isotherm of *n*-octane is 50 mJ/m^2, which is close to the value reported by Aplan *et al.*[6] The nondispersion component of the surface free energy of the same coal calculated from the adsorption isotherm of *n*-propanol is 215 mJ/m^2.

Our studies described in the latest papers,[12,13] carried out on the wettability of coal of various ranks by liquids (of a different part of dispersion and the nondispersion components in its surface tension) did not confirm such a big value of the nondispersion component (γ_S^p) of the surface free energy of coals. These studies[12,13] showed that γ_S^d was nearly the same as reported by Aplan *et al.*[6] and by Staszczuk *et al.*[8] but the γ_S^p value should be smaller than 10 mJ/m^2.

Taking into account the above controversies concerning the surface energy components of coals we think that this problem has not been completely solved. Therefore, we attempted to determine the dispersion and nondispersion components of the surface free energy of Polish coals on the basis of the contact angle measured in systems chosen so that it would be possible to eliminate the influence of the liquid film pressure on the contact angle or to define precisely the changes of the surface free energy of coal under the influence on this film.

For this purpose contact angle measurements were made in the systems: coals of various rank — water drop — *n*-alkanes and analysis of values of the contact angle[7] in the systems: coals of various rank — air bubbles or *n*-alkanes drop — water.

THEORY

Dispersion and nondispersion components of the surface free energy of solids may be calculated, among other things, on the basis of contact angle measurements in suitably chosen systems.[14-23] Such systems may be 1) solid — air bubble — water, 2) solid — hydrocarbon drop — water and 3) solid — water drop — hydrocarbon. The equilibrium state in solid — air buble — water system may be estimated by the Young equation in the form:

where: $\gamma_{SV} = \gamma_S - \pi e$, γ_{SV} is the surface free energy of the solid covered with a water film, πe is the value of changes of the solid surface free energy (γ_S) caused by water film pressure, γ_{SW} is the interfacial free energy os solid-water, γ_W is the surface tension of water, Θ is the contact angle measured through water phase.

For the solid — hydrocarbon drop — water system the equilibrium state is described by the Young equation in the form:

$$\gamma_{SVH} - \gamma_{SW} = \gamma_{WH} \cos \Theta^* \tag{2}$$

where: $\gamma_{SVH} = \gamma_{SH} - \pi e_1$, γ_{SVH} is the interfacial free energy of solid/water film — hydrocarbon, πe_1 is the value of the changes of interfacial free energy of solid-hydrocarbon (γ_{SH}) caused by water film pressure on the solid surface, γ_{WH} is the interfacial tension of water-hydrocarbon and Θ^* is the contact angle of a sessile hydrocarbon drop on the solid surface immersed in water.

For the system solid — water drop hydrocarbon the equilibrium state is described by the Young equation in the form:

$$\gamma_{SH} - \gamma_{SfW} = \gamma_{WH} \cos \Theta_1 \tag{3}$$

where: γ_{SfW} is the interfacial free energy of solid/hydrocarbon film-water, Θ_1 is the contact angle of a sessile water drop on the solid surface immersed in hydrocarbon.

Aronson *et al.*[24] found that in quartz-hydrocarbon drop — water system a durable water film was formed between the surface of the quartz and *n*-tetradecane drop. The thickness of this film is comparable with the water film between quartz and air bubble in quartz — air bubble — water system if the disjoining pressure is the same.[25] Applying this statement to other systems we may assume that $\pi e \approx \pi e_1$.

Taking it into account and using the geometric mean to express the interfacial free energy of solid-hydrocarbon as a function of the dispersion components of the surface free energy of solid and hydrocarbon[14,15] from Eqs. (1) and (2) we obtain the expression:

$$(\gamma_S^{d})^{1/2} = \frac{\gamma_W \cos \Theta - \gamma_{WH} \cos \Theta^* + \gamma_H}{2\,(\gamma_H^{d})^{1/2}} \tag{4}$$

Thus, measuring the contact angle in solid — air bubble — water and solid — hydrocarbon drop — water systems the dispersion components of the surface free energy may be calculated from Eq. (4). The nondispersion components of the surface free energy may be calculated from Eq. (1) or (2) if we can define precisely the value of πe or πe_1.

Our studies on wettability of quartz and marble[26-28] have shown that a water film is formed on these solids, whose pressure changes from γ_S to γ_W. Assuming that $\gamma_S - \pi e \rightarrow \gamma_W$, for the system described by Eq. (1), and using the geometric mean for the dispersive[14-17] and nondispersive[16-18] intermolecular interaction at solid-water interface we may rewrite Eq. (1) in the form:

$$\gamma_S^{p} - 2\sqrt{\gamma_S^{p}\,\gamma_W^{p}} + \gamma_S^{d} - 2\sqrt{\gamma_S^{d}\,\gamma_W^{d}} + \gamma_W \cos \Theta = 0 \tag{5}$$

where γ_S^d, γ_W^d, γ_S^p and γ_W^p are the dispersion and nondispersion components of the surface free energy of the solid (γ_S) and water γ_W, respectively.

The dispersion component of the surface free energy may be calculated from Eq. (4). The nondispersion component of the surface free energy may be calculated from Eq. (5) if the condition $\gamma_S - \pi e = \gamma_W$ is fulfilled.

The dispersion and nondispersion components of the solid surface free energy may be calculated from the contact angle of the water drop on solid surface immersed in two hydrocarbons whose surface tensions (γ_{H_1} and γ_{H_2}) are markedly different.[23] Assuming, after Tamai *et al.*[23], that the nondispersion interactions at solid-water interface for two different hydrocarbons are equal, and using the geometric mean of dispersive intermolecular interactions at solid-hydrocarbon interface, Eq. (3) may be transformed into:

$$(\gamma_S^d)^{1/2} = \frac{(\gamma_{H_1} - \gamma_{H_2}) - (\gamma_{WH_1}\cos\Theta_1 - \gamma_{WH_2}\cos\Theta_2)}{2\,(\sqrt{\gamma^d_{H_1}} - \sqrt{\gamma^d_{H_2}})} \tag{6}$$

where: index »1« and »2« refer to two different hydrocarbons. In the cases where the hydrocarbon film occurs under a water drop in solid — water drop — hydrocarbon system and the dispersive[14–19] and nondispersive[16–18,22] intermolecular interactions may be expressed by the geometric mean, we may write:

$$\gamma_{WH}\cos\Theta_1 = \gamma_H - \gamma_W + \pi e_2 - 2\sqrt{\gamma_S^d\,\gamma_H^d} + 2\sqrt{(\gamma_S^d - \pi e_3)\,\gamma_W^d} + 2\sqrt{(\gamma_S^p - \pi e_4)\,\gamma_W^p} \tag{7}$$

where: πe_3 and πe_4 are the values of the change of the dispersion and nondispersion components of the solid surface free energy, caused by the hydrocarbon film.

The nondispersion component of the solid surface free energy may be calculated from Eq. (7) if the value of γ_S^d is known and we can estimate the value of $\pi e_2 = \pi e_3 + \pi e_4$.

Eq. (7) may be easily solved in two cases: first, when it is possible to assume that $\pi e_2 = 0$ and then, when $\pi e_4 = 0$, and $\pi e_2 = \pi e_3 \to \gamma_S^d - \gamma_H^d$.

EXPERIMENTAL

Contact angles were measured at 20 °C ± 0.1 °C by the sessile drop method using the microscope-goniometer system at magnification × 25. For the contact angle measurements various coal ranks were chosen. These coals originated from the collieries: Siersza, Jankowice, Gotwald, Kleofas, Szczygłowice, Marcell and Gliwice, the ranks of which according to the polish classification[29] were: 31.1, 31.2, 32.1, 32.2, 33, 34 and 35, respectively. A comparison of the Polish classification[29] of coal with ASTM[30] is difficult because they are based on quite different principles.

All coal specimens were carefully selected, excluding those with cracks, mineral matter, different macerals, particles of pyrite, occlusions *etc.* Then the most regular coal specimens were examined under the microscope. The selected pieces were stored for a few months in a desiccator filled with a mixture of molecular sieves (4 Å + 5 Å).

After that, the pieces were roughly polished with emery paper, obtaining a size of about 2 × 2 × 1 cm. Next, for a given piece a plane parallel to the bedding plane was chosen and it was polished in air. Polishing was performed slowly by hand to avoid local overheating and oxidations. The pieces were polished with a series of emery paper (Carborundum grif from 400 to 00). The final polishing was made with white typewriting paper until reflecting surfaces was obtained. All polishing operations were carried out in a special chamber filled with molecular sieves mixture (4 Å + 5 Å).

After polishing the coal plates were placed in a beaker filled with a hydrocarbon and it was placed in ultrasonic bath for 10 minutes. Next, the plates were immersed in the same fresh hydrocarbon in a quartz cell for 2 hours and then they were placed into the measuring chamber.

On thus prepared plates contact angles were measured in the systems: coals of various rank — water drop — *n*-hexane, *n*-dodecane and *cis*-decalin.

In the earlier stage of contact angle measurements it appeared that the obtained results strongly depended on the way a drop settled on a surface of the coal plate. A little shock changed the value of the contact angle, sometimes even by about 20 or 30 degrees. Therefore, we decided to measure the contact angle in two ways. First, a 2 mm^3 water drop was very carefully settled on the surface of the coal plate at a distance from this surface and the contact angle was read out on both sides. Next, on the same plate the second, the third and other following drops of water were settled (of course each drop in a different place), and the contact angle was read out in each case on both sides of each drop.

When the contact angles on the right and left sides of the drops differed by more than 2°, the results were rejected. This procedure of contact angle measurement was repeated for all the studied systems at least for ten different plates (for a given coal rank). On analyzing the results obtained in this way, it appeared that about 90% for each rank lay within an interval of 4°. The average value of contact angles for a given coal rank lying in this interval is called the maximal contact angle (Θ_{max}).

The second way of contact angle measurements differed from the first one only in the procedure of water drop settling. In this case 2 mm^3 water drops were settled on the surface of the coal plate at a higher but constant distance from this surface and sometimes a settling drop was trapped, as Aplan *et al.* reported.[6]

However, this time discrepancies among the contact angle results were higher and about 85% of the obtained values lay in the 4° interval. The average value of a contact angle for a given coal rank lying in this interval is called the minimal contact angle (Θ_{min}).

RESULTS AND DISCUSSION

The average values of contact angles denoted as Θ_{max} and Θ_{min} for the studied systems are listed in Tables I and II, respectively.

TABLE I

Maximal Values of Contact Angles (Θ_{max}) for Water Drops Settled on the Surface of Coals Immersed in: n-*Hexane,* n-*Dodecane and* cis-*Decalin and Values of the Dispersion and Nondispersion Components of the Surface Free Energy Calculated from Eqs (6) and (8), Respectively*

Various rank of coals	Hexane 1			Dodecane 2			*cis*-Decalin 3			Average values	
	Θ_{max}	γ_s^d	γ_s^p	Θ_{max}	γ_s^d	γ_s^p	Θ_{max}	γ_s^d	γ_s^p	γ_s^d	γ_s^p
31.1	139.5	50.0	0.51	145.8	51.9	0.52	149.4	50.9	0.51	50.9	0.51
31.2	141.6	46.5	0.41	147.5	48.8	0.42	150.6	47.6	0.41	47.6	0.41
32.1	140.6	59.0	0.44	148.9	47.0	0.39	151.7	53.0	0.44	53.0	0.42
32.2	143.7	42.9	0.33	149.1	51.3	0.35	152.9	46.9	0.32	47.0	0.33
33	141.9	55.7	0.35	149.3	64.2	0.40	156.0	59.6	0.37	59.8	0.37
34	141.0	62.5	0.37	150.1	64.6	0.38	157.1	63.5	0.37	63.5	0.37
35	142.2	55.3	0.35	150.1	56.6	0.35	155.2	55.8	0.35	55.8	0.35

TABLE II

Minimal Values of Contact Angles (Θ_{min}) for Water Drops Settled on the Surface of Coals Immersed in: n-*Hexane,* n-*Dodecane and* cis-*Decalin and Values of the Dispersion and Nondispersion Components of the Surface Free Energy of Coal Calculated from Eqs (6) and (8), Respectively*

Various rank of coals	Hexane 1			Dodecane 2			*cis*-Decalin 3			Average values	
	Θ_{min}	γ_S^d	γ_S^p	Θ_{min}	γ_S^d	γ_S^p	Θ_{min}	γ_S^d	γ_S^p	γ_S^d	γ_S^p
31.1	107.4	59.0	5.49	112.5	53.9	5.42	115.3	56.5	5.50	56.5	5.47
31.2	108.6	53.4	5.18	113.1	58.5	5.25	116.4	55.8	5.18	55.9	5.20
32.1	110.7	68.7	4.48	117.0	64.5	4.42	121.0	66.6	4.48	66.6	4.46
32.2	111.2	64.8	4.39	117.1	62.6	4.37	120.9	63.7	4.39	63.7	4.38
33	109.2	77.1	4.73	116.3	67.5	4.66	120.6	72.4	4.78	72.3	4.74
34	113.1	68.4	3.79	119.5	85.2	3.98	125.7	76.3	3.80	76.6	3.86
35	112.8	70.4	3.82	119.4	90.4	4.04	126.1	79.8	3.83	80.2	3.90

Table I shows that the Θ_{max} values are in the ranges from 139.5° to 143.7°, 145.8° to 150.1° and 149.4° to 157.1° for coal ranks from 31.1 to 35 immersed in *n*-hexane, *n*-dodecane and *cis*-decalin, respectively.

The highest Θ_{max} values are for coals immersed in *cis*-decalin, and the lowest for coals immersed in *n*-hexane. The biggest difference in Θ_{max} values is for coal rank 34, and it sometimes reaches 16° (see Table I). It can also be seen from Table I that the changes of contact angles (Θ_{max}) for the studied coals immersed in hydrocarbons are small. The changes for *n*-hexane and dodecane did not exceed 5°, and for *cis*-decalin the difference was 7.7°.

The minimal values of contact angles (Θ_{min}) are in the ranges from 107.4° to 113.1° and 112.5° to 119.5° and 115.3° to 126.1° for the studied coals immersed in *n*-hexane, *n*-dodecane and *cis*-decalin, respectively. The measured Θ_{min} values as in the case of Θ_{max} are lowest for coals immersed in *n*-hexane and the highest for coals immersed in *cis*-decalin. The biggest differences among Θ_{min} values for all coal ranks immersed in *n*-hexane, *n*-dodecane and *cis*-decalin are 5.7°, 7.0° and 10.8°, respectively. It should be emphasized that the difference between Θ_{min} of coal of the same ranks immersed in *n*-hexane and *cis*-decalin (Table II) is smaller than for Θ_{max} (Table I). The differences between the values of Θ_{min} (Table II) and Θ_{max} (Table I) is in the range from 27.9° (coal rank of 34 — water droplet — *n*-hexane) to 35.4° (coal rank of 33 — water droplet — *cis*-decalin).

Assuming that the nondispersive interactions at interface of coal — *n*-hexane, coal — *n*-dodecane and coal — *cis*-decalin *are* the same after Tamai *et al.*[23] and using the results listed in Tables I and II, the dispersion component of the surface free energy of the studied coals may be calculated from Eq. (6). Thus, using Eq. (6) we calculated the γ_S^d values for coal ranks from 31.1 to 35, employing in calculations the values of Θ_{max} (Table I) and Θ_{min} (Table II), as well as literature values[31,32] of the surface tension of hydrocarbons ($\gamma_{H(1,2)}$) and water-hydrocarbons interface tension (Table III).

TABLE III

Values of the Surface Tension of Water, cis*-Decalin and Homological Series of Hydrocarbon from* n*-Hexane to* n*-Hexadecane and Values of the Interfacial Tension of Water-Hydrocarbons*[14,31,32]

Liquid	γ_H	γ_{WH}	Various rank of coals						
			31.1	31.2	32.1	32.2	33	34	35
			Θ^*	Θ^*	Θ^*	Θ^*	Θ^*	Θ^*	Θ^*
Hexane	18.49	51.10	85.4	85.5	94.4	96.1	110.3	111.4	114.0
Heptane	20.30	51.10	86.3	86.7	97.2	98.8	112.5	114.3	116.3
Octane	21.80	51.00	87.2	88.1	99.0	99.9	114.0	116.2	117.5
Nonane	22.91	51.02	88.9	88.7	99.8	102.0	114.3	117.5	118.7
Decane	23.90	51.10	88.8	89.9	101.5	103.2	115.1	117.6	120.3
Undecane	24.70	51.10	88.7	90.2	102.5	103.4	119.3	120.5	121.6
Dodecane	25.08	51.12	88.7	90.2	102.0	104.5	117.6	121.0	122.1
Tridecane	25.38	51.14	89.3	91.0	101.4	104.2	118.2	120.8	121.6
Tetradecane	25.60	51.20	89.6	91.4	102.2	102.8	117.8	121.0	122.6
Pentadecane	25.80	51.20	89.3	90.3	102.7	103.0	119.3	120.2	123.1
Hexadecan	26.35	51.22	90.2	91.1	103.1	105.6	119.7	121.1	122.4
cis-decalin	32.18	52.00							
Water	γ_W	γ_W	Θ	Θ	Θ	Θ	Θ	Θ	Θ
	72.8	21.8	48.1	48.6	51.8	52.2	56.0	56.5	57.0

Values of the contact angles:

[a] measured by us in various coal ranks-hydrocarbon-water system,[7]

[b] measured by us in various coal ranks-air bubbles-water system.[7]

Values of $\gamma_S{}^d$ were calculated for all possible combinations of the hydrocarbons used, *i. e.* 1) *n*-hexane — *n*-dodecane, 2) *n*-dodecane — *cis*-decalin and 3) *n*-hexane — *cis*-decalin. The $\gamma_S{}^d$ values calculated from Θ_{max} and Θ_{min} for these combinations of hydrocarbons are given in Tables I and II, respectively. It can be seen from Table I that the $\gamma_S{}^d$ values (calculated from Θ_{max} values) for the coals studied are in the range: 1) from 41.5 mJ/m^2 (coal rank 31.2) to 62.5 mJ/m^2 (coal rank 34), 2) 47.0 mJ/m^2 (coal rank 32.1) to 64.6 mJ/m^2 (coal rank 34) and 3) 46.9 mJ/m^2 (coal rank 32.2) to 63.5 mJ/m^2 (coal rank 34) calculated for three early reported combinations of hydrocarbons. The average $\gamma_S{}^d$ values for the examined coals are in the range from 47 mJ/m^2 (coal rank 32.2) to 63.5 mJ/m^2 (coal rank 34).

The dispersion components of the surface free energy of low-energetic coals (coal ranks 31 and 32) is somewhat smaller than for high-energetic coals (coal ranks 34 and 35). For all the coals examined here the average $\gamma_S{}^d$ value is 53.9 mJ/m^2 and it is higher by about 14 mJ/m^2 than $\gamma_S{}^d$ determined from the adsorption isotherm of *n*-octane on the surface of coal from the Lublin Coal Basin.[8] This average value is also greater by about 9 mJ/m^2

than that of γ_S^d determined by Aplan *et al.*[6] on the basis of the contact angle measurements for methylene iodide on the surface of various coals and than the value determined by us[12] for the same ranks of coal from contact angle measurements of various liquid.

As seen from Tables I and II, the γ_S^d values calculated from Θ_{max} are smaller than those calculated from Θ_{min}. Appropriate γ_S^d values calculated from Θ_{min} for the pairs of hydrocarbons reported earlier 1) *n*-hexane — *n*-dodecane, 2) *n*-dodecane — *cis*-decalin and 3) *n*-hexane — *cis*-decalin are in the ranges: 1) 53.4 mJ/m^2 (coal rank 31.2) to 77.1 mJ/m^2 (coal rank 33), 2) 53.9 mJ/m^2 (coal rank 31.1) to 90.4 mJ/m^2 (coal rank 35) and 3) 55.8 mJ/m^2 (coal rank 31.2) to 79.8 mJ/m^2 (coal rank 35). Hence, the average values of γ_S^d calculated from Θ_{min} are in the range from 55.9 mJ/m^2 to 80.2 mJ/m^2. Table II shows that in contrast to the γ_S^d values listed in Table I the γ_S^d values increase as the rank of coal changes from 31.1 to 35.

Taking into account the γ_S^d values, we may divide the coals studied into three groups: 1) coal rank 31, 2) coal rank 32 and 3) coal ranks 33, 34 and 35. In this case, as it can be seen from Tables I and II, the γ_S^d values markedly differ from those reported by Aplan *et al.*[6] as well as from our earlier results[12] obtained for the same coal ranks.

Therefore, one may ask why such different contact angle values are measured for coals of the same ranks and in the same system and why we obtained such different γ_S^d values from the measured Θ_{max} and Θ_{min} in the same systems.

Eq. (6), used here for the calculation of γ_S^d of coals, was derived by Tamai *et al.*[23] with, the assumption that there is no hydrocarbon film under a water droplet settled on the surface of the solid immersed in hydrocarbons (H_1 and H_2) as well as that nondispersive interactions at solid — water interface in hydrocarbons H_1 and H_2 are the same. In turn, our earlier studies[33] did not exclude the possibility that a hydrocarbon film may occour under a water droplet in solid — water droplet -- hydrocarbon system.

The question whether a hydrocarbon film may be present under a water droplet may be answered by solving Eq. (7). Assuming that no hydrocarbon film exists under the water droplet and that $\pi e_2 = \pi e_3 + \pi e_4 = 0$, Eq. (7) can be transformed into:

$$(\gamma_S^p)^{1/2} = \frac{\gamma_{WH}\cos\Theta_1 + \gamma_W - \gamma_H + 2\,(\gamma_S^d)^{1/2}\,[(\gamma_H^d)^{1/2} - (\gamma_W^d)^{1/2}]}{2\,(\gamma_W^p)^{1/2}} \tag{8}$$

Nondispersion components of the surface free energy of the studied coals were calculated by putting into Eq. (8) the value of Θ_{max} (Table I) or Θ_{min} (Table II) instead of Θ_1 and values of γ_{WH}, γ_H, γ_W, and γ_W^p (Table III) from literature.[14,27] The γ_S^d values used for calculations of γ_S^p were those the average values of which were figured out from Eq. (6) for the three combinations of hydrocarbons used earlier.

The γ_S^p values calculated from Eq. (8) by using Θ_{max} or Θ_{min} are listed in Tables I and II, respectively. The γ_S^p values shown in Table I show that they are in the range from 0.32 mJ/m^2 (coal rank of 32.2 for *cis*-decalin) to 0.51 mJ/m^2 (coal rank of 31.1 for *cis*-decalin) for the studied coals. Hence, it appears that the value of nondispersive interactions at coal-water interface does not depend on the kind of hydrocarbon in which coal plates were immersed to measure $\Theta_{\max}$ and the rank of coal.

In the case of using $\Theta_{\min}$ (for calculations of the $\gamma_S{}^p$) (Table II) one cannot see any great differences in the values of $\gamma_S{}^p$ (Table II) of the studied coal ranks. The $\gamma_S{}^p$ values are in the range from 3.79 mJ/m^2 (coal rank 34 for *n*-hexane) to 5.50 mJ/m^2 (coal rank 31.1 for *cis*-decalin).

The $\gamma_S{}^p$ for coal ranks 31.1 and 31.2 are a little bigger in comparison with those for the other studied coal ranks. We did not find any correlation between the coal ranks and the changes of $\gamma_S{}^p$ calculated from $\Theta_{\min}$.

The results of the $\gamma_S{}^p$ presented in Table II also confirmed the assumption of Tamai *et al.*[23] that nondispersive interactions at solid-water interface are identical regardless of the kind of hydrocarbons in which the solid was immersed. The $\gamma^p{}_S$ values for a given coal rank are nearly equal for the used hydrocarbons (Tables I and II).

It should be emphasized that the $\gamma_S{}^p$ values calculated from Eq. (8) using $\Theta_{\min}$ are very close to those we previously figured out[12] applying another method.

From the comparison of the $\gamma_S{}^p$ values inserted in Tables I and II it appears that the $\gamma_S{}^p$ values calculated from $\Theta_{\min}$ (Table II) are ten times higher than those calculated by using $\Theta_{\max}$ (Table I). This may suggest, according to our earlier studies,[33] that in the coal water droplet-hydrocarbon system one cannot exclude the existence of hydrocarbon film under the water droplet at least in the case of the water droplet settled very carefully on the coal surface. Hence, the resulting $\gamma_S{}^d$ and $\gamma_S{}^p$ values calculated from Eqs. (6) and (8) by using $\Theta_{\max}$ may be a little smaller.

In order to verify the $\gamma_S{}^d$ and $\gamma_S{}^p$ values calculated from Eqs. (6) and (8) on the basis $\Theta_{\max}$ and $\Theta_{\min}$, we calculated these values for the studied coals using Eqs. (4) and (5).

In these calculations we used the contact angle values measured in the system coals — air bubble (Θ — Table III) or hydrocarbon droplet (Θ^* — Table III) — water[7] and the literature values of γ_W, γ_H and γ_{WH} which are also listed in Table III.[14,31,32] The contact angles Θ^* were measured for droplets of hydrocarbons in the homological series from *n*-hexane to *n*-hexadecane. The $\gamma_S{}^d$ calculated from Eq. (4) and $\gamma_S{}^p$ calculated from Eq. (5) are listed in Table IV. To calculate the $\gamma_S{}^p$ values we used the $\gamma_S{}^d$ calculated from Eq. (4) and the contact angles measured in coal — air bubble — water system. The values of $\gamma_W = 72.8$, $\gamma_W{}^d = 21.8$ and $\gamma_W{}^p = 51$ mN/m were taken from literature.[14]

It should be emphasized that Eq. (5) is a quadratic one and for each $\gamma_S{}^d$ value we obtain two different values of $\gamma_S{}^p$. Table IV shows that for the given coal rank similar values of $\gamma_S{}^d$ were obtained using 11 aliphatic hydrocarbons, and for the studied coal ranks from 31.1 to 35 the dispersion components of the surface free energy increased from 53.2 mJ/m^2 to 83.6 mJ/m^2.

TABLE IV

Values of the Dispersion and Nondispersion Component of Coal Surface Free Energy Calculated from Eqs (4) and (5), Respectively

Liquid	Various rank of coals													
	31.1		31.2		32.1		32.2		33		34		35	
	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p	γ_s^d	γ_s^p
Hexane	53.7	127.2 9.03	53.0	129.2 8.51	61.5	128.8 8.60	63.5	127.7 8.90	80.1	117.8 11.77	80.9	118.2 11.64	84.3	114.9 12.71
Heptane	53.0	127.9 8.85	53.1	129.1 8.54	63.4	126.7 9.16	65.2	125.7 9.42	80.0	117.9 11.73	81.9	116.8 12.09	84.0	115.3 12.57
Octane	52.9	128.0 8.82	53.4	128.8 8.65	64.1	125.9 9.37	64.8	126.2 9.29	79.5	118.6 10.51	81.8	116.9 12.04	82.8	117.0 12.00
Nonane	54.3	126.6 9.19	53.3	128.9 8.59	64.0	126.0 9.34	66.7	124.0 9.91	78.1	120.5 10.95	82.0	116.6 12.14	82.7	117.2 11.95
Decane	53.4	127.5 8.95	54.1	128.1 8.79	65.5	124.3 9.83	67.3	123.3 10.12	77.9	120.8 10.84	80.6	118.6 11.51	83.5	116.0 12..33
Undecane	52.7	128.2 8.77	54.0	128.2 8.77	66.1	123.6 10.03	67.0	123.6 10.01	82.3	114.6 12.79	83.5	114.5 12.85	84.1	115.2 12.61
Dodecane	52.5	128.4 8.72	53.7	128.5 8.69	65.0	124.9 9.65	67.8	122.6 10.29	79.8	118.2 11.64	83.6	114.3 12.90	84.2	115.0 12.66
Tridecane	53.0	127.9 8.85	54.5	127.7 8.90	63.9	126.1 9.31	67.1	123.5 10.05	80.2	117.6 11.82	82.9	115.3 12.56	83.0	116.8 12.09
Tetradecane	53.0	127.9 8.92	54.9	127.3 9.00	64.8	125.1 9.60	65.0	126.0 9.36	79.5	118.6 11.51	83.0	115.2 12.61	84.1	115.2 12.61
Pentadecane	52.8	128.1 8.80	53.4	128.8 8.65	65.3	124.5 9.76	65.0	126.0 9.36	81.2	116.2 12.27	81.5	117.3 11.91	84.5	114.6 12.81
Hexadecane	53.6	127.3 9.00	54.1	128.1 8.79	65.3	124.5 9.76	68.2	122.2 10.43	81.0	116.5 12.18	82.0	116.6 12.14	82.8	117.0 12.00
Average values	53.2	127.7 8.90	53.8	128.4 8.72	64.4	125.5 9.49	66.1	124.6 9.74	80.0	117.9 11.64	82.1	116.4 12.22	83.6	115.8 12.39

Taking into account the average values of γ_S^d, the studied coals may be divided into three groups, *i. e.*: 1) coal ranks 31.1 and 31.2; 2) coal ranks 32.1 and 32.2; and 3) coal ranks 33 , 34 and 35. Coals within the same groups possessed similar values of the dispersion components of their surface free energy. The data in Table IV aslo show that the γ_S^d calculated from Eq. (4) are practically equal to those calculated from Eq. (6) using Θ_{min} (Table II). Differences between the γ_S^d values did not exceed 5.5 mJ/m^2, except for coal rank 33 (γ_S^d — 72.3 and 80 mJ/m^2). In the case of the γ_S^d calculated from Eq. (6) but using Θ_{max} the difference reached 27.8 mJ/m^2 for coal rank 35.

From Table IV it also results that lower γ_S^p values are in the range from 8.51 mJ/m^2 to 12.81 mJ/m^2 and the higher ones from 114.3 mJ/m^2 to 129.2 mJ/m^2.

It appears that the lower γ_S^p values are from 1.5 to 3 times bigger than those calculated from Eq. (8) (Table II), and they are almost the same as it was reported.[12] However, the higher γ_S^p values are nearly twice as low as those calculated on the basis of the adsorption isotherm of *n*-propanol for coal from the Lublin Coal Basin.[8]

The differences among γ_S^p values for each rang of coal calculated on the basis of measured contact angles in the systems coal — water drop — hydrocarbon (Table II) and coal — air bubble — water (lower — Table IV) probably result from the existence of a hydrocarbon film under the water drop. This film can retard polar interactions between coal and water. Hence the γ_S^p values calculated from Eq. (8) (Table II) are lower.

As regards the other values of γ_S^p (higher — Table IV), we think that they are rather too high for coal because it is very difficult to find a realistic explanation for such high values which are only a consequence of algebraic solution of Eq. (5). However, additional studies should be made to clarify this point.

On the basis of the calculations presented above we can also conclude that the surface free energy of the studied coals resulted from the dispersive and nondispersive interface interactions, which supports our earlier studies.[12,13] However, in contrast to the earlier suggestions,[5,6,12,13] we think that the surface free energy of coal depends on its rank.

The presence of water molecules on coal surface can probably show »a real picture« of the surface free energy of the studied coals, which was indicated by Staszczuk[34] in his studies of coal properties using the method of thermal analysis.

The value of the critical surface tension of wetting of the studied[5] coals is 45 mJ/m^2 and is equal to the critical surface tension of wetting of quartz and iron ores.[11] It is commonly known that the surface of these solids is highly hydrated and the value of the surface free energy distinctly exceeds its critical surface tension of wetting.

From the performed calculations it can also be concluded that for the coals studied the nondispersion components of the surface free energy are practically the same and in our opinion the most proper value should be about 10 mJ/m^2 or less. This component may result from the existence of such polar groups as hydroxyl, carboxyl, carbonyl *etc.* on coal surface.

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SAŽETAK

Kvasivost površine ugljena i pripadne komponente površinske slobodne energije

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Mjereni su kontaktni kutovi za sisteme: različite vrste ugljen/vodena kap/*n*-heksan, *n*-dodekan ili *cis*-dekalin. Iz dobivenih rezultata izračunane su disperzijske i nedisperzijske komponente površinske slobodne energije različitih vrsta ugljena iz Poljske.

Te vrijednosti (γ_s^d i γ_s^p) uspoređene su s vrijednostima izračunanima na temelju mjerenja kontaktnih kutova provedenih ranije za sisteme: ugljen/mjehurić zraka ili kap ugljikovodika/voda. Dobiveni rezultati ukazuju na to da površinska slobodna energija ugljena potječe iz disperzijskih i nedisperzijskih međumolekulskih interakcija, a da disperzijska komponenta te energije ovisi o vrstama ugljena. Vrijednost nedisperzijskih komponenata površinske slobodne energije ne ovisi o vrsti ugljena i ne prelazi vrijednost 10 mJ/M^2.

Na temelju tih rezultata može se zaključiti da razlog neslaganjima u vrijednostima površinske slobodne energije ugljena što su ih dobili razni autori, može biti prisutnost vodenog filma na površini ugljena. Vodeni film može također biti razlogom što su razni autori dobili gotovo jednake vrijednosti za površinsku slobodnu energiju za različite vrste ugljena.