

Interpretation of the wetting contact angle in the system various coal ranks—liquid drop—air

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Measurements of the contact angle in the systems various coal ranks—water drop—air and various coal ranks—methylene iodide drop—air were carried out. Then, for the systems studied an analysis of the equilibrium state was made on the basis of the modified Young equation (taking into account all possible factors influencing the contact angle).

We have found that the surface Gibbs energy of various coal ranks results from both dispersive and nondispersive intermolecular interactions and its value depends on the coal rank. It was also stated that the surface of coal is heterogeneous, which leads to the differences of the contact angle values for a given coal rank. These differences were smaller for higher coal ranks. The calculations carried out suggest that the existence of water film on the coal surface does not only change its surface Gibbs energy but also the ratio of the dispersion values to those of the nondispersion components.

Проведено измерение величины краевого угла в системах: различные виды угля—капля воды—воздух и различные виды угля—капля йодистого метилена—воздух. Для изучаемых систем, далее, проведен анализ равновесного состояния на основании модифицированного уравнения Янга (с учетом всех возможных факторов, влияющих на величину краевого угла).

Обнаружено, что поверхностная энергия Гиббса различных видов угля складывается как из дисперсионных, так и недисперсионных межмолекулярных взаимодействий, и ее значение зависит от вида угля. Установлено также, что поверхность угля является гетерогенной, что приводит к различным величинам краевого угла для данного вида угля. При улучшении качества угля эти различия уменьшались. Произведенные расчеты позволяют предположить, что наличие водной пленки на поверхности угля ведет не только к изменению поверхностной энергии Гиббса, но и к изменению соотношения дисперсионных и недисперсионных компонентов.

Coal is partially produced as fines which are generated by modern mining operations and transportations. In many cases the amount of fines may be as high as 30 % of the overall coal output. Fines may be used as a source of energy

or chemical substances after their beneficiation. The most commonly used technique for this purpose is froth flotation the effectiveness of which, among other things, depends on coal surface properties closely connected with its surface Gibbs energy.

Therefore, many studies are undertaken to determine the surface Gibbs energy of various coal ranks, the values of which are different and depend on the methods used and the interpretation of the results obtained [1—8]. Most of the methods used are based on measurements of contact angles. The interpretation of contact angle data is difficult and in many cases it is based on approximations and assumptions. *Aplan et al.* [3], interpreting the contact angles in the system coal ranks—liquid drop—air assumed that in this system dispersive interfacial (coal—liquid) interactions are only present. They also suggest that the adsorption film of such liquids as methylene iodide and water on the surface of coal does not change its surface Gibbs energy. Moreover, we assumed [1] that in the systems coal ranks—hydrocarbon drop—water and coal ranks—air bubble—water water film occurs under hydrocarbon drops or air bubbles and that this film, according to *Aronson et al.* [9], decreases the surface Gibbs energy of coal by the same value in both systems. It was concluded that the surface Gibbs energy of coals cannot result only from dispersive intermolecular interactions. This is in agreement with the fact that different kinds of polar groups [10, 11] exist on the surface of various coal ranks, and we cannot exclude the influence of π -bonding on the interactions between the surface of coal and the adherent phase [5].

The differences in the interpretations of the contact angles measured in the systems including coal may lead to various conclusions concerning both the source of the surface Gibbs energy of coal and its value [1—8]. Therefore, we have attempted to make a more detailed analysis of the equilibrium state of the systems solid—methylene iodide drop—air and solid—water drop—air. These systems are very often used to determine the surface Gibbs energy of solids. We have also made proper measurements of the contact angles for methylene iodide and water on the surface of Polish coal of various ranks.

Theoretical

The equilibrium state in the solid—liquid drop—air systems, in which there does not exist a liquid film at solid—liquid phase boundary, is described by the Young equation in the form

$$\gamma_S - \gamma_{SL} - \Pi_e = \gamma_L \cos \Theta \quad (1)$$

where γ_S is the surface Gibbs energy of solid, γ_L is the liquid surface tension, γ_{SL} is the interfacial surface Gibbs energy of solid—liquid, Π_e is the value of changes

of the surface Gibbs energy of solid caused by the liquid film beyond the liquid drop and Θ is the contact angle.

Dividing the surface Gibbs energy of solid and liquid into two components — dispersion (γ^d) and nondispersion (γ^n) [12—14], and expressing γ_{SL} as a function of the geometric mean of dispersive [12—19] and nondispersive [15—17, 19] intermolecular interactions, from eqn (1) we obtain [13]

$$\gamma_L \cos \Theta = -\gamma_L + 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^n \gamma_L^n} - \Pi_e \quad (2)$$

where γ_S^d , γ_S^n , γ_L^d , and γ_L^n are dispersion (γ^d) and nondispersion (γ^n) components of the surface Gibbs energy of solid (γ_S) and liquid (γ_L), respectively.

From eqn (2) the dispersion component of the surface Gibbs energy of a solid may be calculated if $2\sqrt{\gamma_S^n \gamma_L^n} = 0$ and $\Pi_e \approx 0$ [20]. Then eqn (2) may be written

$$(\gamma_S^d)^{1/2} = \frac{\gamma_L(\cos \Theta + 1)}{2(\gamma_L^d)^{1/2}} \quad (3)$$

Such calculations may also be carried out for $\gamma_S^n = 0$ or when $\gamma_S - \Pi_e \rightarrow \gamma_L$ [21, 22]; then from eqn (2) we obtain

$$\gamma_S^d - 2\sqrt{\gamma_S^d \gamma_L^d} + \gamma_L \cos \Theta = 0 \quad (4)$$

The nondispersion components of the solid surface Gibbs energy may be calculated from eqn (2) if the γ_S^d value is known and $\Pi_e \approx 0$ [21] or $\gamma_S - \Pi_e \rightarrow \gamma_L$. For $\Pi_e = 0$ eqn (2) may be transformed into the form

$$(\gamma_S^n)^{1/2} = \frac{\gamma_L(\cos \Theta + 1) - 2\sqrt{\gamma_S^d \gamma_L^d}}{2(\gamma_L^n)^{1/2}} \quad (5)$$

Eqn (2) for $\gamma_S - \Pi_e \rightarrow \gamma_L$ [21, 22] may be rewritten

$$\gamma_S^n - 2\sqrt{\gamma_S^n \gamma_L^n} + \gamma_S^d - 2\sqrt{\gamma_S^d \gamma_L^d} + \gamma_L \cos \Theta = 0 \quad (6)$$

The dispersion and nondispersion components of surface Gibbs energy of a low energetic solid ($\gamma_S \leq \gamma_L$; $\Pi_e \approx 0$) could be simultaneously determined from eqn (2) if the contact angle was measured at least for two liquids the values of dispersion and nondispersion components of the surface tension of which are different. Solving eqn (2) for two liquids, with respect to γ_S^d , we obtain [23]

$$(\gamma_S^d)^{1/2} = \frac{\gamma_{L_1}(\cos \Theta_1 + 1) - \sqrt{\gamma_{L_1}^n / \gamma_{L_2}^n} \gamma_{L_2}(\cos \Theta_2 + 1)}{2(\sqrt{\gamma_{L_1}^d} - \sqrt{\gamma_{L_1}^n \gamma_{L_2}^d / \gamma_{L_2}^n})} \quad (7)$$

where index 1 and 2 refer to two liquids. The nondispersion components of the surface Gibbs energy may be calculated from eqn (5), calculating previously the dispersion components.

From the practical point of view the most suitable pair of liquids for deter-

mination of the solid surface Gibbs energy from contact angle values is that of methylene iodide and water. Methylene iodide is an organic liquid having a high surface tension value which in 99.25 % results from dispersive intermolecular interactions. The dispersion component of the surface tension of methylene iodide is equal to 50.42 mN m^{-1} [23], and this value is one of the highest among the $\gamma_{\text{L}}^{\text{d}}$ values of liquids used for measurements of contact angles (mercury is exception) [12]. The surface tension of water is by 21 mN m^{-1} higher than that of methylene iodide [12, 23] and in 29.95 % it results from dispersive, and in 70.05 % from nondispersive intermolecular interactions ($\gamma_{\text{W}}^{\text{d}} = 21.8 \text{ mN m}^{-1}$, $\gamma_{\text{W}}^{\text{n}} = 51 \text{ mN m}^{-1}$) [12]. So, methylene iodide may be considered as an apolar and water as a strong polar liquid.

In our opinion this pair of liquids is most suitable for determination of $\gamma_{\text{S}}^{\text{d}}$ and $\gamma_{\text{S}}^{\text{n}}$. Using the values of $\gamma_{\text{L}}^{\text{d}}$ and $\gamma_{\text{L}}^{\text{n}}$ and γ_{L} of these liquids in eqns (6) and (7) we obtain the values of solid surface Gibbs energy components which are loaded with the least error.

Experimental

Measurements of contact angles of methylene iodide and water on coal plates were carried out at 20°C by the sessile drop method using the microscope-goniometer system at 25-fold magnification.

The samples of coal of various ranks used in these experiments originated from Polish collieries: Siersza (31.1), Jankowice (31.2), Gottwald (32.1), Kleofas (32.2), Szczygłowice (33), Marcel (34), and Gliwice (35). The numbers in brackets denote the rank of coal according to the Polish classification [24]. The methyl iodide was from Lachema, Brno. Before measurements of contact angle all coal ranks were carefully selected, excluding those with cracks, mineral matters, different macerals, present particles of pyrite, occlusions, *etc.* Then most regular coal specimens without a trace of contamination were examined under the microscope. The selected pieces were stored for a few months in a desiccator filled with a mixture of molecular sieves (0.4 nm—0.5 nm).

Afterwards the pieces were roughly polished with emery paper, obtaining a size about $2 \times 2 \times 1 \text{ cm}$. Next, for a given piece a plane parallel to the bedding plane was chosen and it was polished in air. The polishing was performed slowly by hand to avoid a local overheating and oxidations. The pieces were polished with a series of emery paper (Carborundum grit from 400 to 00). The final polishing was made with white typewriting paper until reflecting surface was obtained. All polishing operations were carried out in a special chamber filled with molecular sieves mixture (0.4 nm—0.5 nm).

The prepared plate of coal was placed in the measuring chamber filled with saturated vapour of the liquids studied an hour before measurements of the contact angle. A 2 mm^3 liquid drop was settled and the contact angle was immediately read out several times on both sides of the drop. The reproducibility of contact angle measurements was $\pm 1^{\circ}$. When the contact angle on the right and left side of the drop differed more than 2° such results were rejected.

The contact angle for each rank of coal was measured at least on 30 coal plates and the number of the contact angles obtained was higher than 100 because a few drops of water or methylene iodide were settled on each plate.

Results and discussion

From measurements of the contact angle of the systems coal—methylene iodide drop—air and coal—water drop—air for a given coal rank and liquid we have obtained a set of values of contact angles. The smallest and the highest values of each set and the average contact angle values are listed in Table 1 (columns 1—4), which we have denoted as Θ_{\min} , Θ_{\max} , and Θ_A , respectively.

It appears from Table 1 that the measured Θ_{\min} and Θ_{\max} values (columns 1 and 3) practically do not depend on coal ranks. However, the average Θ_A value (columns 2 and 4) increases from coal rank of 31.1 to 33 and then it decreases for coal ranks of 34 and 35. Such behaviour of Θ_A suggests that there should exist a relationship between the coal rank and its wettability by water and methylene iodide. To make it more visible, three exemplified distribution series of contact angles measured for water drops placed on the surface of coal ranks 31.1 (curve 1), 33 (curve 2), and 35 (curve 3) were constructed, which are shown in Fig. 1.

For a given coal rank the whole variation interval was divided into class intervals of 2° , and for each class interval a fraction of Θ value (in %) was calculated. Each curve in Fig. 1 represents the relationship between the fraction of Θ (%) and the average value of a given class interval. From Fig. 1 it appears that all curves have a maximum, which proves that the statistical methods may be used for interpretation of these results. It should be emphasized that maxima are almost equal to the average values of the contact angle denoted as Θ_A (Table 1, column 2). With the increase of the coal rank from 31 to 35 the maximum of the class interval of the contact angle (Fig. 1) values is shifted from Θ_{\min} to Θ_{\max} values.

Analyzing all experimental data it should be emphasized that the shapes of the curves obtained for water and methylene iodide for a given coal are almost the same. On the basis of the results presented, exemplified in Fig. 1, the above-mentioned conclusion that the wettability of coal depends on its rank was confirmed. However, for both the studied systems coal—water drop—air and coal—methylene iodide drop—air, unequivocal description of the equilibrium state is difficult on the basis of measured contact angles. Therefore, we shall examine with a great care all possible solutions of the previously presented equations (see Theoretical) using these values of contact angle.

Aplan et al. [2, 3] and *Sablik* [4, 5] suggested that the surface Gibbs energy of the studied coals originates only from dispersive intermolecular interactions.

Table 1

Measured values of contact angle of water and methylene iodide on the surface of various coal ranks and calculated dispersion and nondispersion components of the surface Gibbs energy of these coals

Coal rank	Water		Methylene iodide		Methylene iodide	Water
	$\Theta_{\min} - \Theta_{\max}$	Θ_A	$\Theta_{\min} - \Theta_{\max}$	Θ_A	$\frac{\gamma_s^d}{\text{mJ m}^{-2}}$	$\frac{\gamma_s^d}{\text{mJ m}^{-2}}$
					Eqn (3)	Eqn (3)
	1	2	3	4	5	6
31.1	62.8—82.9	74.9	10.1—12.6	11.1	50.4—50.0	129.0—76.7
31.2	69.8—87.2	77.8	13.2—24.2	14.9	49.8—46.8	110.0—66.9
32.1	73.1—82.2	80.5	18.1—28.1	20.7	48.7—45.3	101.3—78.4
32.2	73.9—88.8	80.3	15.2—28.3	21.9	49.4—45.2	99.2—63.4
33	73.2—90.8	84.1	20.1—27.2	25.1	48.1—45.7	101.0—59.1
34	74.2—86.6	83.5	17.4—22.8	22.5	48.9—47.3	98.4—68.2
35	72.3—85.8	83.1	18.2—24.7	23.3	48.7—46.6	103.4—69.8

Table 1 (Continued)

		Methylene iodide	Water	From Θ_A			
γ_s^d mJ m ⁻²	γ_s^n mJ m ⁻²	γ_s^d mJ m ⁻²	γ_s^d mJ m ⁻²	γ_s^d ^a mJ m ⁻²	γ_s^n ^b mJ m ⁻²	γ_s^d ^a mJ m ⁻²	γ_s^n ^b mJ m ⁻²
Eqn (7)	Eqn (5)	Eqn (4)	Eqn (4)	Eqns (2) and (6)	Eqns (2) and (6)	Eqns (2) and (6)	Eqns (2) and (6)
7	8	9	10	11	12	13	14
47.92	3.61	59.9–64.3	—	57.5–66.9	0–2.38	58.3	2.05
47.46	2.79	65.3–83.2	79.9	59.8–84.9	0–2.88	70.6	0.46
46.15	2.24	73.3–89.7	—	73.3–90.9	0–2.75	79.4	0.36
45.74	2.35	68.6–90.0	84.2	68.6–91.5	0–2.58	81.3	0.47
45.02	1.52	76.5–88.2	89.2	76.5–89.7	0–2.56	86.3	0.26
45.89	1.55	72.2–80.9	78.3	72.2–82.7	0–1.63	82.0	0.17
45.56	1.68	73.5–84.0	76.2	73.5–85.7	0–2.35	83.4	0.25

a) The $\gamma_s^d < 72.8 \text{ mJ m}^{-2}$ values were calculated from pair equation obtained by introducing Θ for methylene iodide into eqn (2) (for $\Pi_c = 0$) and Θ for water into eqn (6), and $\gamma_s^d \geq 72.8 \text{ mJ m}^{-2}$ values were calculated from pair equation introducing Θ for methylene iodide and Θ for water into eqn (6). *b*) The γ_s^n values were calculated from eqns (2) and (6) or only from eqn (6) for given γ_s^d values, respectively (see *a*)).

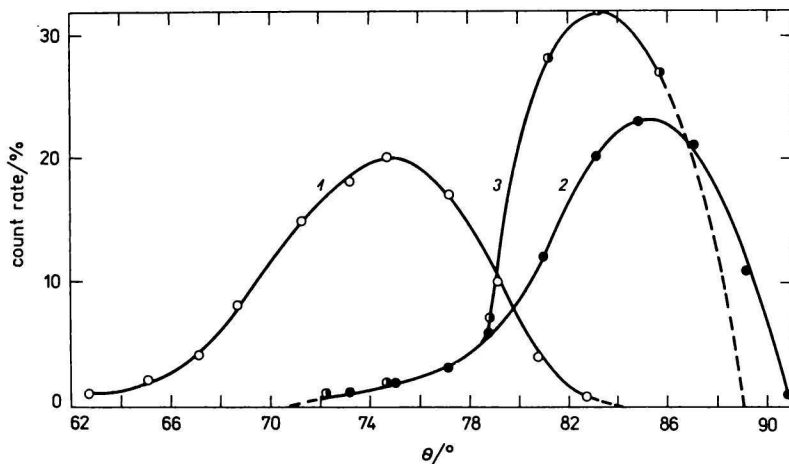


Fig. 1. Percentage distribution of the contact angle values measured in the system coal—water drop—air for the coal rank of 31.1 (1), 33 (2), and 35 (3).

The average value of γ_S^d for American coal is 45 mJ m^{-2} [3]. Taking it into account we may think that an equilibrium state in the coal—water drop—air and coal—methylene iodide drop—air systems will be described by eqn (3) because for $\gamma_S^n = 0$ and $\gamma_S \leq \gamma_L$ we may assume that $\Pi_e \approx 0$ [12]. If it is true, then by solving eqn (3) for the measured values of Θ we should obtain the same γ_S^d value as *Aplan et al.* [3]. Using for water $\gamma_W = 72.8 \text{ mN m}^{-1}$, $\gamma_W^d = 21.8 \text{ mN m}^{-1}$, $\gamma_W^n = 51 \text{ mN m}^{-1}$ and for methylene iodide $\gamma_D = 50.8 \text{ mN m}^{-1}$ [25], $\gamma_D^d = 50.42 \text{ mN m}^{-1}$, and $\gamma_D^n = 0.38 \text{ mN m}^{-1}$ [23] and Θ_{\min} and Θ_{\max} from Table 1 (columns 1 and 3) we calculated the γ_S^d values and inserted them in Table 1 (columns 5 and 6).

The γ_S^d values, as shown in Table 1 (column 5), calculated for contact angles Θ_{\min} and Θ_{\max} of methylene iodide are practically the same for all coal ranks and they are equal to the value reported by *Aplan et al.* [3]. However, the γ_S^d values of the studied coals calculated from Θ_{\min} and Θ_{\max} for water, clearly differ between them and in some cases the differences are higher than 100% (Table 1, column 6). The γ_S^d values calculated from Θ_{\min} for water are twofold or many times higher than those of methylene iodide (Table 1, columns 5 and 6). The same differences among the γ_S^d values calculated from Θ_{\max} are smaller and they do not exceed 50% (Table 1, columns 5 and 6).

In conclusion, as shown in Table 1, the γ_S^d value calculated from eqn (3) for Θ_{\min} and Θ_{\max} measured in the systems a given coal rank—water drop—air, differed clearly from those obtained by *Aplan et al.* [3]. The disagreement between γ_S^d values calculated from the contact angle of methylene iodide and

water may be an evidence that $\gamma_s^n \neq 0$ or $\Pi_e \neq 0$, or both these values are higher than zero.

Assuming that $\gamma_s^n = 0$, but $\Pi_e = \gamma_s - \gamma_L$ [21, 22] the γ_s^d values of the studied coal ranks were calculated from eqn (4) and they are listed in Table 1 (columns 9 and 10). We did not take into account the values of $\gamma_s^d < 50.8 \text{ mJ m}^{-2}$ for methylene iodide and $\gamma_s^d < 72.8 \text{ mJ m}^{-2}$ for water.

As shown in Table 1 (columns 9 and 10), the differences among the γ_s^d values calculated from eqn (4) are smaller than those obtained from eqn (3) for both liquids used. It should be stressed that eqn (4) has no solution for a few measured contact angle values (the γ_s^d did not possess a physical meaning), and no relationship was found between the γ_s^d and the studied coal ranks. So, one can think that nondispersive intermolecular interactions may influence the contact angle values. The more so, as it is most probable that there are different kinds of polar groups and π -bonding [5, 10, 11] on the surface of coal.

Thus, taking into consideration the above facts in the studied systems, three cases of the equilibrium state may be distinguished:

1. Values of the contact angle of water and methylene iodide do not depend on the film pressure of these liquids on coal surface.
2. Values of the contact angle of methylene iodide depend on its film pressure but not on water film pressure.
3. Values of the contact angle of water and methylene iodide depend on the film pressure of these liquids on coal surface.

In the first case ($\Pi_e \approx 0$) the γ_s^d and γ_s^n values for the studied coal ranks may be calculated from eqns (7) and (5). Using Θ_A values for water and methylene iodide and the above-mentioned values of γ_w , γ_w^d , γ_w^n , γ_D , γ_D^d , and γ_D^n , the γ_s^d values for these coal ranks were calculated from eqn (7), and next γ_s^n from eqn (5) and listed in Table 1 (columns 7 and 8). As it can be seen from Table 1 (columns 7 and 8), the surface Gibbs energy components γ_s^d and γ_s^n do not depend on the coal ranks studied. As this case was previously described [6] we do not discuss it in details.

For the second and third case eqn (2) may be solved if $\gamma_s - \Pi_e \rightarrow \gamma_L$ [21, 22]. Such assumption may only be used for one, (coal—water drop—air) or for both studied systems (coal—methylene iodide drop—air and coal—water drop—air). Assuming that in the case of water and methylene iodide $\gamma_s - \Pi_e \rightarrow \gamma_L$ the dispersion and nondispersion components of the surface Gibbs energy of the studied coal ranks may be calculated from eqn (6), however, some difficulties may arise because for a given coal rank we obtain two series of contact angle values (from Θ_{\min} to Θ_{\max} — see Table 1). The first series is obtained for methylene iodide and the second for water. Because of coal surface heterogeneity we do not know which pair of contact angles for water and methylene iodide corresponds to the same value of coal surface Gibbs energy, therefore, we

carried out calculations from eqn (6) employing all possible pairs of contact angle of 0.5° interval (in the range of Θ_{\min} to Θ_{\max}). In some cases it appeared that the obtained $\gamma_s^d + \gamma_s^n = \gamma_s$ values were lower than 72.8 mJ m^{-2} . For such cases calculations were carried out from eqns (2) and (6), respectively, assuming that for water $\Pi_c \approx 0$ (in eqn (2)). On the basis of these calculations intervals of γ_s^d and γ_s^n for each coal rank were established and listed in Table 1 (columns 11 and 12). In the same way we also calculated γ_s^d and γ_s^n for the studied coals using Θ_A values, and they are inserted in Table 1 (columns 13 and 14).

As can be seen from Table 1, the dispersion components of the surface Gibbs energy of the studied coal ranks are in the range from 60 to 90 mJ m^{-2} , and the nondispersion components are in the range from 0 to 3 mJ m^{-2} . Taking into consideration for a given coal rank all measured values of the contact angle for water and methylene iodide, we did not find any relationship between the coal ranks and their surface Gibbs energy. However, taking into account γ_s^d calculated from Θ_A , these values were found to increase up to coal rank of 33, but for the rank of 34 and 35 they decreased a little. The γ_s^n component for the studied coal ranks is not large, which practically does not depend on the coal rank and it is comparable to γ_L^n for aliphatic alcohols [26].

Conclusion

On the basis of the conducted measurements and calculations it may be stated that the surface of the studied coal ranks is heterogeneous and their surface Gibbs energy results from dispersive and nondispersive intermolecular interactions. The heterogeneity of the coal surface depends on the coal rank. Higher ranks of coal (33, 34, and 35) are more homogeneous than the low ones (31 and 32). A relationship between the average surface Gibbs energy of coal and its rank was also found.

It seems that some discrepancies of views concerning coal surface Gibbs energy may result from not taking into account the existence of water film on the coal surface. This film can not only decrease the coal surface Gibbs energy but it also can change the ratio of γ_s^d to γ_s^n . The existence of water film on the surface of coal may be the reason that the value of its surface Gibbs energy [2, 3] as well as the critical surface tension of wetting [4–6] was equal to 45 mJ m^{-2} for all the coal ranks studied. This value is also equal to γ_C obtained by *Bernett* and *Zismann* [27] for high energetic polar solids covered with water film. Since in our calculations the influence of the film of a liquid on the contact angle value has been taken into consideration, the values of γ_s determined by us are different from those taken from the literature. However, this conclusion should be confirmed by using other methods.

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