Influence of n-alkanes and diacetonyl alcohol on the detachment force of air bubbles detached from a low-rank coal surface

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Measurements of the force of detachment of air bubbles from the surface of coal of rank 31.1 and 31.2 precovered with n-alkane in the homologous series from n-hexane to n-hexadecane were carried out in 0 to 10 mass % aqueous solution of diacetonyl alcohol. Using the contact angle values measured earlier in the same system the detachment force was also calculated. On the basis of measurements and calculations we stated that the detachment force depend on the thickness of n-alkane film precovering the coal surface, the kind of n-alkane and diacetonyl alcohol concentration. The most profitable conditions for creating a stable connection of coal/n-alkane film—air bubble in diacetonyl alcohol solution were found with a thick n-alkane film at 1 % solution of diacetonyl alcohol. A good agreement between the measured and calculated values of the detachment force for the systems studied was also shown.

Проведено измерение силы прилипания пузырей воздуха к поверхности угля ряда 31,1 и 31,2, покрытой н-алканами гомологического ряда от н-гексана до н-гексадекана в водных растворах диацетонового спирта от 0 до 10 % по массе. Используя значения угла смачивания, измеренные ранее в этой же системе, были также вычислены значения силы прилипания. Исходя из измерений и расчетов, мы установили, что сила прилипания зависит от толщины пленки н-алкана, покрывающей поверхность угля, типа н-алкана и концентрации диацетонового спирта. Было найдено, что наиболее выгодными условиями для образования устойчивого сцепления уголь/пленка н-алкана—воздушный пузырь в растворе диацетонового спирта являются толстая н-алкановая пленка в 1 % растворе диацетонового спирта. Демонстрируется также хорошее совпадение измеренных и рассчитанных значений силы прилипания в изучаемых системах.

On both macroscopic and microscopic scales coal is a complex heterogeneous material composed of organic and inorganic matter. The organic matter of coal consists of macerals such as: vitrinite, exinite, and inertinite. The inorganic matter in coals belongs to two broad classes, namely, the discrete mineral matter, and minor and trace elements. The discrete mineral matter is usually present as particles larger than 1 μm in size. The major discrete minerals in coals are: clays, quartz, gypsum, calcite, dolomite, and pyrite [1, 2].

From the industrial point of view these minerals are highly undesirable and delimit the utilization of coal. A high demand for coal on the one hand and the protection of the environment on the other hand cause that the mineral matter must be removed from the organic matter to the highest degree.

One of the methods to achieve this purpose is froth flotation for which mineralization of air bubbles [2—5] is an elementary act. A decisive factor of an effective beneficiation of coals is stability of air bubble—coal grain aggregates. The stability of the aggregates may be assessed by measuring the force of detachment of air bubbles from the surface of coal grains [3, 6]. Such measurements may be helpful for establishing a criterion of the flotation reagents, using low ranks of coal for flotation enrichment. In the previous papers [7, 8] we showed the influence of nonpolar and polar liquids on the stability of coal—air bubble aggregates. For flotation of coals both nonpolar and polar reagents are used [2, 3] and their common action determines the efficiency of the process.

Therefore, it seemed interesting to investigate the influence of n-alkanes and diacetonyl alcohol (4-methyl-4-hydroxy-2-pentanone) on the stability of the systems mentioned above. For this purpose measurements of the force of detachment of air bubble from the surface of coal of rank 31.1 and 31.2 precovered with n-alkanes were carried out in 0 to 10 mass % aqueous solution of diacetonyl alcohol.

Experimental

Coals used for studies of the stability of coal/n-alkane film—air bubble—aqueous solution of diacetonyl alcohol system originated from Siersza and Jankowice collieries and their ranks, according to the Polish classification [9], were 31 1 and 31.2, respectively.

The samples of the coal ranks were carefully selected under the microscope excluding those with cracks, mineral matters, different macerals, particles of pyrite, oclussions, *etc.* The most regular pieces of coal were additionally tested under the microscope and they were placed for a few months in a desiccator filled with a mixture of molecular sieves (4A + 5A). The coal pieces were then polished using the method described earlier [10]. From the coal plates very thin lamellae with one polished side were split off and cut into small grains 2 mm × 2 mm in size. The grains were attached using paraffin to a quartz rod before its calibration by means of a cathetometer [6] and the rod with grain was carefully immersed into the hydrocarbon studied. The coal grain was then taken out from hydrocarbon and hydrocarbon excess was removed by shaking and washing several times in double distilled water. Afterwards the grain was washed with aqueous solution of diacetonyl alcohol of a given concentration. The grain—rod aggregate was put in the measuring vessel filled with a given diacetonyl alcohol solution. Next, the coal grain was contacted with an air bubble of 4.046 mm in diameter which was pushed out of a capillary by means of a micrometer screw and the detachment force was measured by the method described earlier [11, 12]. According to this method the values of the detachment force were read out under the microscope from the deviation of the quartz rod. Then the air bubble was removed and a new one of the same size was pushed out from the capillary and contacted with the same grain surface and the detachment force was measured again. Such a measurement procedure was repeated for 33 air bubbles. After that time air bubbles were only contacted with the surface of coal grain and removed from it without measuring the detachment force, which was not measured until for the hundredth air bubble.

The measurement procedure was used for both ranks of coal (31.1 and 31.2) precovered with a film of n-alkanes in a homologous series from n-hexane to n-hexadecane. The aqueous solution of 0.5 to 10 mass % diacetonyl alcohol was used (measurements for clean water were made earlier).

For a given system coal/n-alkane film—air bubble—aqueous solution of diacetonyl alcohol the measurements of the detachment force were made at least for five coal grains, at the temperature of $(20 \pm 0.1)\,°C$ and the measurement error was $\pm 5 \times 10^{-4}$ mN.

Results and discussion

The force of detachment of an air bubble from the surface of coal of both ranks (31.1 and 31.2) precovered with a given hydrocarbon is a decreasing function of the number of disrupted air bubbles for a given concentration of diacetonyl alcohol. These changes are more dependent on n-alkane precovered coal surface, the concentration of diacetonyl alcohol and the coal ranks.

In Fig. 1 the detachment force of an air bubble detached from the surface of coal of rank 31.1 precovered with n-hexane (curve *1*), n-undecane (curve *2*), and hexadecane (curve *3*) at 1 mass % (*a*) and 10 mass % (*b*) solution of diacetonyl alcohol is presented as an example.

Fig. 1*a* shows that in 1 % diacetonyl alcohol solution the detachment force (F_0) decreases rapidly with the increasing number of air bubbles (n) detached from the coal surface precovered with n-hexane (curve *1*), so that for the 17th air bubble F_0 becomes a constant value. The biggest drop of F_0 occurs for the first five air bubbles. The course of curves F_0 as a function of n for coal surface precovered with n-undecane (curve *2*) and n-hexadecane (curve *3*) is completely different. F_0 values for coal surface precovered with n-undecane slightly increase for the first four air bubbles, then for the next seven ones F_0 decreases sharply. Further increase of the number of air bubbles detached from coal surface causes a slight decrease of F_0 to a constant value for the 17th air bubble. For coal of 31.1 rank precovered with n-hexadecane F_0 slightly increases to a maximal value which is reached for the 6th air bubble. The course of the corresponding

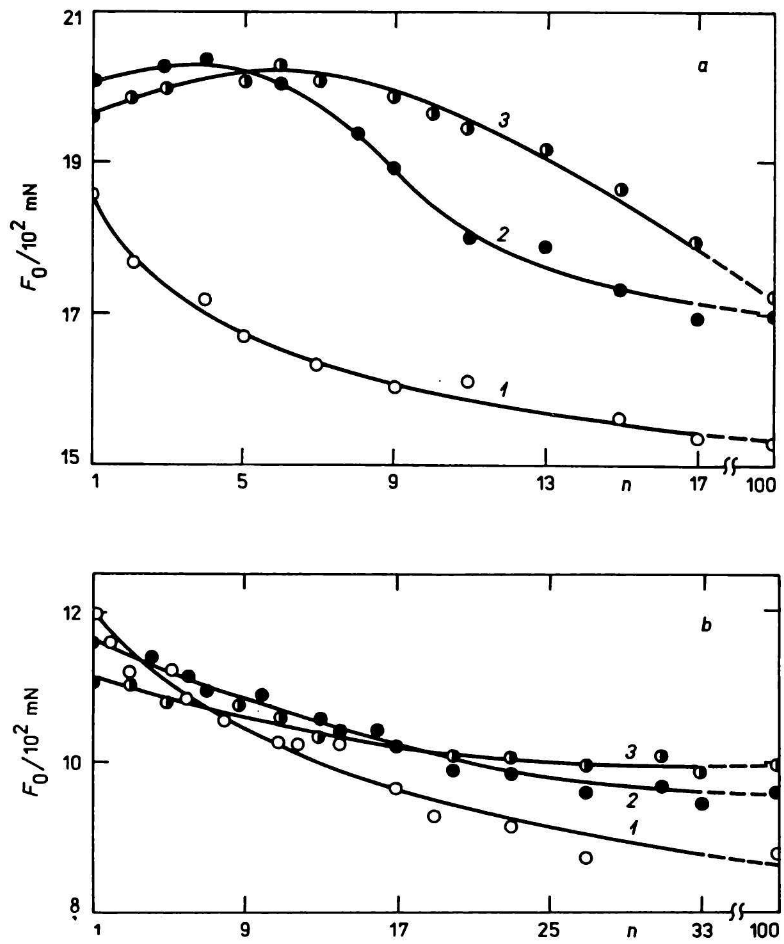
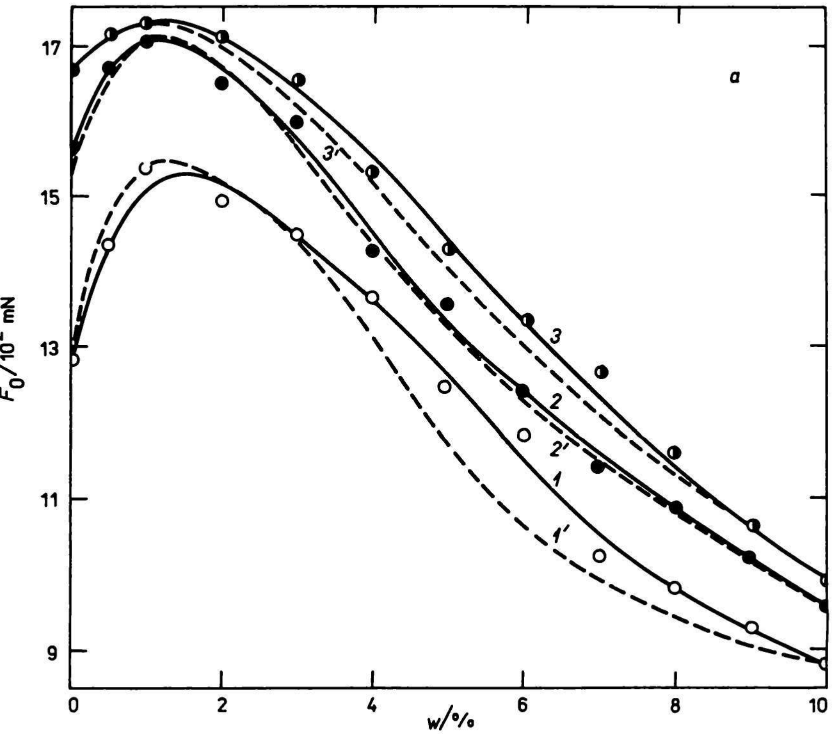


Fig. 1. The relationship between the force of detachment of an air bubble from the surface of coal of rank 31.1 precovered with n-hexane (curve *1*), n-undecane (curve *2*), and n-hexadecane (curve *3*) in 1 mass % (*a*) and 10 mass % (*b*) solution of diacetonyl alcohol and the number of air bubbles.

Fig. 2. The relationship between the force of detachment for the hundredth air bubble from the surface of coal of ranks 31.1 (*a*) and 31.2 (*b*) precovered with n-hexane (curve *1* and *1'*), n-undecane (curve *2* and *2'*), and n-hexadecane (curve *3* and *3'*) and the mass fraction of diacetonyl alcohol. Curves *1*, *2*, and *3* for measured F_0 values, curves *1'*, *2'*, and *3'* for F_0 values calculated from eqn (*1*).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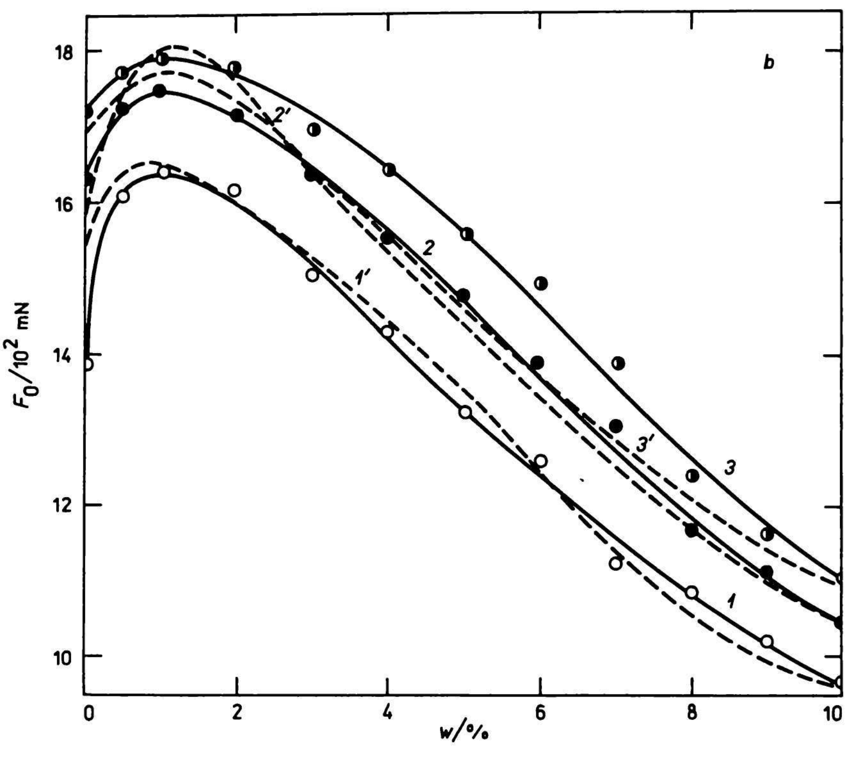
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curve *3* (Fig. 1*a*) for the system is a little different from that of coal/n-undecane film—air bubble—1 % diacetonyl alcohol solution system (Fig. 1*a*, curve *2*). The main difference is that curve *3* runs through a more clear and broader maximum and its decrease is more gentle than the respective values for curve *2*. In general, we may state that constant values of F_0 are obtained for a still larger number of air bubbles detached from the surface of coal of ranks 31.1 and 31.2 when the length of a hydrocarbon chain increases from n-hexane to n-hexadecane. This observation is less visible and the changes of F_0 for a given coal surface precovered with hydrocarbon are smaller when diacetonyl alcohol concentration increases. These statements are confirmed by the results presented in Fig. 1*b*. This figure shows that for coal precovered with n-undecane (curve *2*) and n-hexadecane (curve *3*) the differences between F_0 values for the first and for the hundredth air bubble are smaller than those presented in Fig. 1*a*. For air bubbles contacted with coal surface in 10 % solution of diacetonyl alcohol we did not obtain the maximum on curves of F_0 *vs.* n, but only a progressive decrease of its values and the decrease became smaller as the length of the hydrocarbon chain increased. The values of F_0 for the first air bubbles detached from coal surface in 10 % solution of diacetonyl alcohol were the highest for the coal surface precovered with n-hexane (curve *1*) and the smallest for the coal surface precovered with n-hexadecane (curve *3*). The same sequence of F_0 for n-alkane film is reversible but in 1 % solution of diacetonyl alcohol (Fig. 1*a*).

The influence of diacetonyl alcohol concentration on the detachment force (F_0) for the hundredth air bubble detached from the coal surface precovered with n-hexane (curve *1*), n-undecane (curve *2*), and n-hexadecane (curve *3*) is presented in Figs. 2*a* and 2*b* for coal ranks 31.1 and 31.2, respectively. It is evident that with the increase of the mass fraction (w) of diacetonyl alcohol in water from 0 to 10 % (for $w = 0$ the values of F_0 were taken from the paper [7]) the F_0 values increase to maximum, but a further increase of diacetonyl alcohol concentration causes a sudden decrease of F_0 to the value corresponding to the alcohol mass fraction $w = 10$ %. The courses of the curves F_0 *vs.* w for both coals precovered with n-hexane (curves *1*), n-undecane (curves *2*), and n-hexadecane (curves *3*) are similar, and curve *1* takes the lowest position while curve *3* the highest. It means that for a given diacetonyl alcohol concentration F_0 values for the hundredth air bubble increase from n-hexane to n-hexadecane. This is clearly seen in Figs. 3*a* and 3*b*, where the detachment force (F_0) for the hundredth air bubble in 1 mass % (curves *1*) and 10 mass % (curves *2*) diacetonyl alcohol solution as a function of the number of carbon atoms in n-alkane molecule (C_n) is presented for coal ranks 31.1 and 31.2, respectively.

As can be seen from these figures for the systems coal/n-alkane film—air bubble—1 % solution of diacetonyl alcohol (curves *1*) F_0 value increases stepwise with increasing C_n from n-hexane to n-hexadecane. For another kind of systems involving 10 % solution of diacetonyl alcohol the changes of F_0 values as a function of C_n are nearly linear (curve *2*). So, the increase of diacetonyl alcohol concentration causes disappearance of the difference between the respective films formed by even and odd hydrocarbons. The stepwise changes are observed for many systems [12—16], which is usually explained by a different structure of odd and even hydrocarbon films on a solid surface.

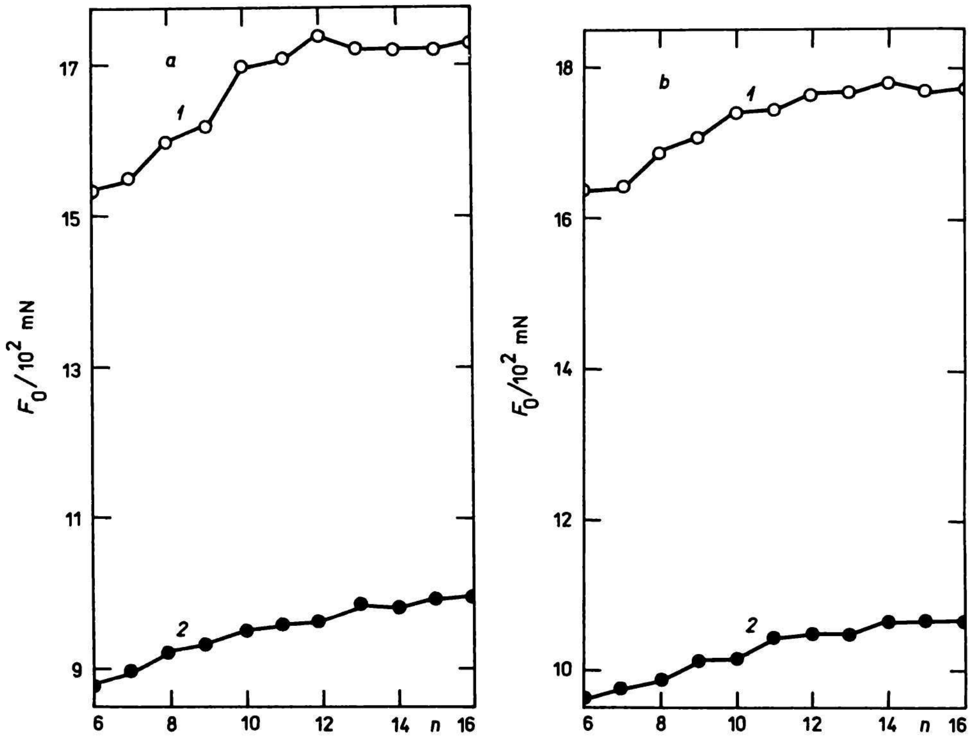

Fig. 3. The relationship between the detachment force for the hundredth air bubble 1 mass % (curve *1*) and 10 mass % (curve *2*) solution of diacetonyl alcohol for coal ranks 31.1 (*a*) and 31.2 (*b*) and the number of carbon atoms in hydrocarbon molecule.

On the basis of the detachment force presented above we may state that the detachment of the following air bubbles from the coal surface precovered with n-alkanes causes thinning of n-alkanes film whereby F_0 value is changed. A resistance to the thinning of films increases with the increase of diacetonyl alcohol concentration and the increase of the number of carbon atoms in n-alkane molecule. From the practical point of view the most profitable conditions for the creation of a stable connection a coal/n-alkane film—air bubble exist for a thick n-alkane film in 1 % solution of diacetonyl alcohol.

It is commonly known that the detachment force F_0 characterizing the stability of a three-phase system: solid—air bubble—liquid should be strictly connected with the wettability of the solid [6, 16, 17]. Then, from the theoretical and practical point of view, it may be interesting to correlate the contact angles measured earlier [18] with the detachment force.

Our earlier examinations [6, 17] have shown that the force of detachment of an air bubble from the surface of minerals depends, among other things, on the contact plane, reaching a maximal value for the so-called critical contact plane $r_{k(k)}$. For the given system the maximal value of the detachment force $F_{0(max)}$ may be calculated from the following equation [17]

$$F_{0(max)} = \pi \, r_{k(k)} \, \gamma_L \sin \Theta \qquad (1)$$

where γ_L is the surface tension of liquid, Θ is the contact angle of solid.

The value of $r_{k(k)}$ may be calculated from the expression [17]

$$r_{k(k)} = \frac{R \sin \Theta}{2} \left[\frac{4}{2 + \frac{3}{2}(4 - \sin^2 \Theta)^{1/2} - \frac{1}{8}[(4 - \sin^2 \Theta)^3]^{1/2}} \right]^{1/3} \qquad (2)$$

where R is the radius of a spherical air bubble.

Using γ_L values for the solution of diacetonyl alcohol from the paper [8] and the contact angle values for the hundredth air bubble measured in the system coal/n-alkane film—air bubble—aqueous solution of diacetonyl alcohol [18] and the values of $r_{k(k)}$ calculated from eqn (*2*) for $R = 2.023$ mm, $F_{0(max)}$ values were calculated from eqn (*1*) and they are depicted in Figs. 2*a* and 2*b* as dotted curves. The $F_{0(max)}$ values presented in these figures were obtained for the surface of coal of ranks 31.1 (Fig. 2*a*) and 31.2 (Fig. 2*b*) precovered with n-hexane (curve *1'*), n-undecane (curve *2'*), and n-hexadecane (curve *3'*).

It is obvious that the course of curves *1'*, *2'*, and *3'* is very similar to that of curves *1*, *2*, and *3*, respectively, and the numerical values of $F_{0(max)}$ calculated and measured are very close to one another. Hence it appears that on the basis of the measured contact angle by the captive air bubble method we may forecast the stability of the coal/n-alkane film—air bubble—aqueous solution of diacetonyl alcohol system for a given thickness of n-alkane film and for a given concentration of diacetonyl alcohol. An agreement between the measured and calculated F_0 values (Figs. 2*a* and 2*b*) for a given system also justified the fact that the detachment of air bubbles both from the coal plate surface and coal grain surface precovered with an n-alkane gives a similar thickness of the film characteristic of a given rank of coal in diacetonyl alcohol solution at any of the given concentrations. On the basis of the studies carried out it is difficult to determine exactly this thickness, therefore, further investigations in this field have to be continued.

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