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## THE EFFECT OF LIQUIDS ON THE INTERACTION BETWEEN COAL PARTICLES

*Received March 5, 2001; reviewed and accepted May 15, 2001*

Taking into account the published earlier values of the destruction time of the coal column structure formed from the four fractions of coal particles having the average diameter  $1.5 \times 10^{-4}$  m,  $2.5 \times 10^{-4}$  m,  $3.5 \times 10^{-4}$  m and  $4.5 \times 10^{-4}$  m in the homologous series of alkanes and alcohols, the correlation between destruction time and bulk properties of coal and liquids as well as the liquid-air, coal-air and coal-liquid interfacial properties was studied. On the basis of this study the linear relationship between the reciprocal destruction time and average diameter of the coal fractions, work of alkane and alcohol cohesion, their density, the difference between liquids and coal density, and free energy of interactions per one molecule of the liquid was found. From these relationships, the critical values of the particles diameter, work of cohesion, density, difference between coal and liquid density, and free energy of interactions for infinitely long destruction time were determined. It was stated that for systems having critical values of these parameters, the detachment force is equal to the attachment one. From study it also results that the attachment forces between coal particles depend on the work of cohesion of liquid and work of adhesion of coal to liquid, and that the destruction of the structure of the sediment column take place as a result of the interruption of the film of the liquid between two coal particles.

*Key words: adhesion, coal particles, alkanes, alcohols, interfacial interactions, attachment and detachment forces*

### INTRODUCTION

Interactions among particles of solid through a liquid play an important role in many technological processes such as: froth flotation, oil agglomeration, shear flocculation, carrier flotation, precipitate flotation, coagulation flocculation (Leja 1982), (Warren 1975), (Sadowski 1993) and (Wójcik et. al. 1978). In these processes an aqueous suspension of mineral particles is mixed with a collector or an immiscible

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liquid, such as kerosene or diesel oil, which consist of different kinds of hydrocarbons. Adsorption or spreading of the collector on the surface of a mineral causes its hydrophobization. Hydrophobic or hydrophobized particles of an ore can be preferentially wetted by an apolar liquid, which forms capillary bridges between the particles, causing thus their aggregation or agglomeration.

Knowledge of the values of the interparticle interactions through a liquid can be helpful to explain more exactly the mechanism of these processes.

Different apparatuses and methods are used to determine adhesive interaction as well as the perimeter of the contact plane between a soft solid sphere and a flat rigid solid surface, or between a hard solid sphere and a flat soft solid surface (Johnson et al. 1971), (Maugis 1992), Derjaguin et al. 1961) and (Derjaguin et al. 1975). The obtained results are discussed on the basis of two main approaches commonly called as Johnson, Kendall and Roberts (JKR) (1971) or Derjaguin, Muller and Toporow (DMT) (1975) theories. In our laboratory in the sixties, a simple device was used to measure the destruction time of the sediment coal structure (Waksmundzki et al. 1965) and (Waksmundzki et al. 1965a).

Using this device the destruction time of the sediment column structure of coal particles was measured in two homologous series of liquids: n-alkanes (Wójcik et al. 2000) and n-alcohols (Wójcik et al. 2000a). The obtained results were interesting, but not explained enough so far. Therefore, the purpose of our paper is to find the correlation between the destruction time and bulk properties of the n-alkanes, n-alcohols, and coal as well as the n-alkanes (n-alcohols)-air, coal-air and coal-n-alkanes (n-alcohols) interfacial properties.

## EXPERIMENTAL

### METHOD

A schematic diagram of the device for measurements of the destruction time of the sediment column structure (Waksmundzki et al. 1965), (Waksmundzki et al. 1965a), (Wójcik et al. 2000), (Wójcik et al. 2000a) and (Wójcik et al. 2000b) is presented in Fig. 1. It consists of a glass tube (1) -0.4m long and a  $3 \cdot 10^{-3}$ m in inner diameter, and a glass vessel  $3 \cdot 10^{-5}$ m<sup>3</sup> in volume (2) connected with the glass tube by a rubber plug (3) so as to move the tube up and down. The glass vessel is closed by a stopper (4). The other end of the tube is closed by a silicone plastics seal tightened by a screw (5).

### MEASUREMENTS

The destruction time of the coal sediment column structure was measured for four size fractions of coal particles whose average diameters were:  $1.5 \cdot 10^{-4}$ m,  $2.5 \cdot 10^{-4}$ m,  $3.5 \cdot 10^{-4}$ m and  $4.5 \cdot 10^{-4}$ m, respectively. The measurements were carried out in n-alkanes, from hexane to hexadecane, and in n-alcohols from methanol to decanol (Wójcik et al. 2000) and (Wójcik et al. 2000a).

Fig. 1

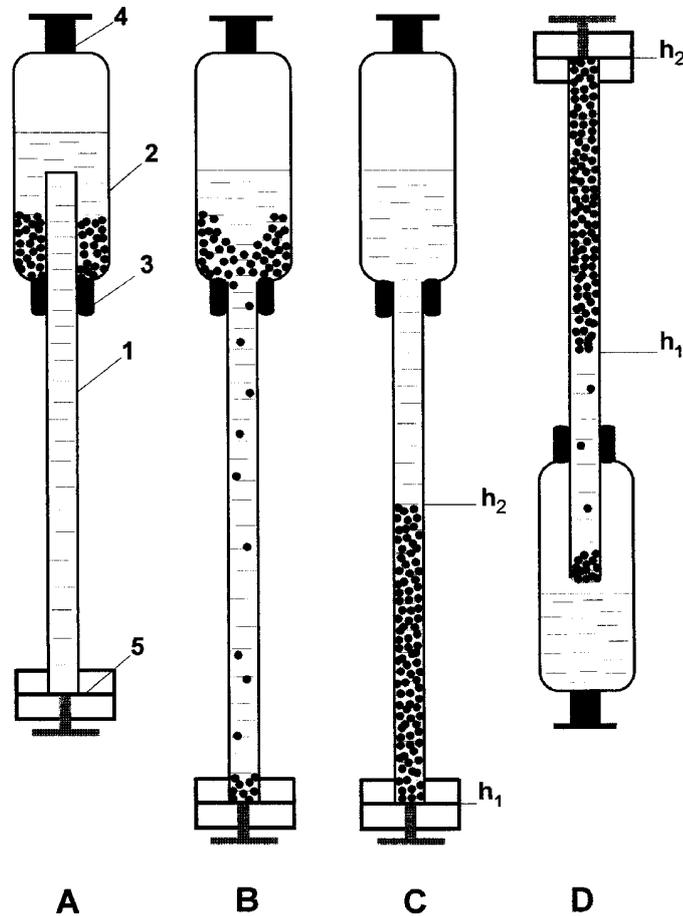


Fig. 1. Schematic diagram of the device for the destruction time measurements: (1) glass tube; (2) glass vessel; (3) rubber plug; (4) stopper; and (5) sealing system. (A) The device filled with the studied suspension; (B) formation of the sediment column; (C) the sediment column formed; (D) destruction sediment column structure.  $h_1$  and  $h_2$  are the bottom and upper levels of the of the sediment column

The sediment column of coal particles was formed in the glass tube by pouring  $2,5 \cdot 10^{-5} \text{ m}^3$  of the liquid in the glass vessel and tube and adding  $2 \times 10^{-3} \text{ kg}$  sample of a given fraction of coal particles (Fig.1A). The tube was moved down, as shown in Fig. 1B, and the particles falling into the tube formed a sediment column, the length of which was ca. 0.3 m between the level  $h_1$  and  $h_2$  (Fig. 1C). Next, the tube was moved up over the level of alkane, and the column structure was established in 10 min. After

that the device was quickly inverted, as shown in Fig. 1D, and the particles detached from the sediment column and dropped to the end of the tube, forming a new sediment column (Fig. 1D).

The destruction time of the coal sediment column structure was measured by a stop-watch, starting when the first coal particle detached from the column at the level  $h_1$  (Fig. 1D), and stopping when the last coal particle started to drop at the level  $h_2$  (Fig. 1D). The procedure of the destruction time measurements was repeated several times for each coal fraction and each liquid used.

## DISCUSSION

We have found that the destruction time increases with increasing length of the hydrocarbon chain of the studied liquids and decreases with increasing diameter of coal particles. This means that the difference between the force of a coal particle attachment to a coal particle through the liquid and the force of a coal particle detachment from a coal particle increases with increasing number of carbon atoms in a molecule of the liquid and decreases with increasing average diameters of coal particles. These findings suggest that the difference between the attachment and detachment forces go to zero as the average diameter of coal particles decreases. Therefore, for certain size of coal particles the destruction time is infinitely long and the particles do not detach from those of the column. The diameter of such particles is called the critical diameter (Waksmundzki et al. 1965), (Waksmundzki et al. 1965a), (Wójcik et al. 2000), (Wójcik et al. 2000a) and (Wójcik et al. 2000b).

We have found linear relationship between the reciprocal of the destruction time and: 1) the average diameter of coal particles fractions, 2) work of cohesion of the liquids, 3) density of the liquids, 4) difference between densities of coal and a studied liquid, 5) reciprocal of the free energy of interaction per molecule of the liquid. These relationships satisfy the equation:

$$1/t = a + bX \quad (1)$$

where:  $t$  is the destruction time,  $a$  and  $b$  are the constants and  $X$  the parameters mentioned above.

The parameters determined from Eq. (1) for the destruction time equal to infinity ( $1/t = 0$ ) were called critical. The critical diameter of coal particles did not depend on length of the hydrocarbon chain of the liquids and average values in alkanes and alcohols is  $9.4 \cdot 10^{-5}$ m and  $9.8 \cdot 10^{-5}$ m, respectively.

The critical work of cohesion of the liquids and their critical density difference practically did not depend on the average diameter of coal particle fractions (Tab. I).

For each studied liquid if the coal particles diameter has critical value, then the detachment force is equal to the attachment one. The same case takes place for all studied fractions of coal particles if the liquid (alkane or alcohol) would have the critical work of cohesion. In these cases coal particles do not detach from one another and the sediment column is stable.

Table I. Critical work of cohesion of alkanes and alcohols and the critical density differences between coal and the liquids

Liquids	Coal size fractions x10 <sup>4</sup> m	Critical work of cohesion in mN/m	Critical density differences $\Delta\rho$ in kg/m <sup>3</sup>
A			
Alkanes	1.5	57.1	556.5
	2.5	57.3	551.3
	3.5	57.5	549.8
	4.5	57.5	549.9
	Average	57.3	551.9
B			
Alcohols	1.5	58.2	505.5
	2.5	58.3	504.3
	3.5	58.5	503.2
	4.5	58.4	503.5
	Average	58.4	504.1

Assuming that coal particles are spheres, the detachment force was calculated from equation (Wójcik et al. 2000) and (Wójcik et al. 2000a)

$$F_D = \frac{1}{6} \Pi d_{cr}^3 g (\rho_C - \rho_L) \quad (2)$$

where  $d_{cr}$  is the critical diameter of coal particles,  $g$  is the acceleration due to gravity;  $\rho_C$  and  $\rho_L$  are the density of coal and liquid, respectively. The calculated  $F_D$  values in alkanes (from hexane to hexadecane) and alcohols (from methanol to decanol) were in the range from  $29.1 \cdot 10^{-10}$  N/particles to  $24.2 \cdot 10^{-10}$  N/particles and from  $26.6 \cdot 10^{-10}$  N/particles to  $24.7 \cdot 10^{-10}$  N/particles (Tab. II), respectively (Wójcik et al. 2000) and (Wójcik et al. 2000a).

Taking into account the critical density difference, the detachment force was calculated from Eq. (2) for alkanes and alcohols and was  $23.5 \cdot 10^{-10}$  N/particle and  $24.4 \cdot 10^{-10}$  N/particle, respectively.

For coal particles having the critical diameter the detachment force can be expressed by the equation

$$F_D = W_{Coh.cr} \cdot L = W_{Coh.cr} \cdot 2\pi R \quad (3)$$

where  $W_{Coh.cr}$  is the critical work of cohesion of the alkane or alcohol,  $L$  is the parameter of the contact plane between two coal particles in the liquid and  $R$  is the radius of the contact plane.

Table II. Detachment ( $F_D$ ) and attachment ( $F_A$ ) forces between two coal particles (in N/particle and in N/m), radius of the contact plane between coal particles ( $R$ ), and the difference between attachment and detachment forces ( $F_D - F_A$ ).

Liquid	$F_D \cdot 10^{10}$ N/particle	$F_D \cdot 10^3$ N/m	$R \cdot 10^{10}$ M	$F_A \cdot 10^{10}$ N/particle	$(F_D - F_A) \cdot 10^{10}$ N/m	$F_A \cdot 10^3$ N/m
A.						
1.Hexane	29.1	57.3	80.9	18.7	10.4	37.6
2.Heptane	28.0	57.3	77.8	19.7	8.3	41.2
3.Octane	27.2	57.3	75.6	20.5	6.7	44.0
4.Nonane	26.9	57.3	74.8	21.5	5.4	46.6
5.Decane	26.1	57.3	72.5	21.7	4.4	48.6
6.Undecane	25.6	57.3	71.1	22.0	3.6	50.2
7.Dodecane	25.2	57.3	70.0	22.4	2.8	51.9
8.Tridecane	24.9	57.3	69.2	22.6	2.3	53.0
9.Tetradecane	24.7	57.3	68.6	22.8	1.9	54.9
10.Pentadecane	24.3	57.3	67.5	22.9	1.4	55.0
11.Hexadecane	24.2	57.3	67.3	23.2	1.0	55.9
12.Average	23.5	57.3	65.3	23.5	0	57.3
B.						
1.Methanol	26.6	58.4	72.6	20.4	6.2	45.1
2.Ethanol	26.7	58.3	72.9	20.5	6.2	45.1
3.Propanol	26.0	58.4	70.9	20.8	5.2	47.1
4.Butanol	25.7	58.4	70.1	21.5	4.2	49.2
5.Pentanol	25.5	58.4	69.6	22.5	3.0	51.8
6.Hexanol	25.2	58.3	68.8	22.6	2.6	52.7
7.Heptanol	25.1	58.4	68.5	23.1	2.0	54.1
8.Octanol	25.0	58.4	68.2	23.4	1.6	55.0
9.Nonanol	24.8	58.3	67.8	23.7	1.1	56.0
10.Decanol	24.7	58.4	67.4	24.0	0.7	57.1
11.Average	24.6	58.4	67.1	24.6	0	58.4

The radius of the contact plane between two coal particles in the studied liquids was calculated from Eq. (3), using the detachment force and critical work of cohesion of alkane and alcohol taken from literature (Wójcik et al. 1978), (Wójcik et al. 2000a) and (Wójcik et al. 2000b). The values of the radius of the contact plane are listed in Tab. II A and B and they decrease with increasing length of the hydrocarbon chain of alkanes from  $80.9 \cdot 10^{-10}$  m to  $67.3 \cdot 10^{-10}$  m and alcohols from  $72.6 \cdot 10^{-10}$  m to  $67.4 \cdot 10^{-10}$  m.

Knowing the detachment force in Newton per particle and the perimeter of the contact plane between two coal particles in the liquid, detachment force in Newton per unit of length was calculated from Eq. (3) and listed in Tab. II. As it is seen the values of the detachment force, for both homologous series of liquids, do not depend on the length of hydrocarbon chain of alkanes and alcohols. The average values for these series of liquids are  $57.3 \cdot 10^{-10}$  N/m and  $58.4 \cdot 10^{-10}$  N/m, respectively. These values are equal to the critical cohesion of alkane and alcohol determined from linear

relationship of the reciprocal of the destruction time as a function of the work of cohesion of the liquid.

The changes of the radius of the contact plane were unexpected to us because the work of cohesion of the studied liquids and their work of adhesion to coal increased with increasing length of the hydrocarbon chain of the liquids. Only the interfacial free energy of the coal–liquid system decreased as a function of the length of hydrocarbon chain of alkanes and alcohols. Therefore, we previously calculated the attachment force of two coal particles through a liquid assuming that the contact plane between them was formed by a constant number of molecules of the studied alkanes or alcohols (Wójcik et al. 2000) and (Wójcik et al. 200a). The values of the attachment force obtained in this way were bigger than those of the detachment force, which would mean that coal particle were not disrupted from the sediment column. To explain this problem the attachment force between two coal particles through the studied liquid was calculated from the equation

$$F_A = W_{Coh} \cdot 2\pi R \quad (4)$$

where  $W_{Coh}$  is the work of the cohesion of the studied liquid,  $R$  is the radius of the contact plane between two coal particles.

The attachment force for the homologous series of alkanes from hexane to hexadecane and alcohols from methanol to decanol is in the range from  $18.6 \cdot 10^{-10}$  N/particle to  $23.1 \cdot 10^{-10}$  N/particle and from  $20.4 \cdot 10^{-10}$  N/particle to  $24.0 \cdot 10^{-10}$  N/particle, respectively as listed in Tab. II A and B, respectively. The attachment force increases with increasing length of the hydrocarbon chain of the liquids which is clearly seen in Fig. 2 A and B where, the attachment and detachment forces as a function of the number of carbon atoms in alkane and alcohol molecules are presented. It appeared that the maximal attachment force was equal to the minimal force (Fig. 2 A and B, Tab. II A and B).

As it is seen in Fig. 2 the difference between the detachment and attachment forces which values are also listed in Tab. I decreases with increasing length of the hydrocarbon chain of the liquids, reaching zero for alkane and alcohol whose work of cohesion is critical. In Fig. 3 A and B the relationship of the reciprocal of the destruction time as a function of the difference between the detachment and attachment forces is plotted. The reciprocal of the destruction time of the coal sediment column structure decreased linearly (Fig. 3) with decreasing difference between the detachment and attachment forces ( $\Delta F$ ).

The curves presented in Fig. 3 should be started from the beginning of the coordinate system because for  $\Delta F = 0$  the reciprocal of the destruction time should be zero. As it is seen in Fig. 3 for  $1/t = 0$  the difference between the detachment and attachment forces is smaller than zero. It is evident that the attachment force results not only from the work of cohesion of the liquid but also from the work of adhesion of coal-liquid.

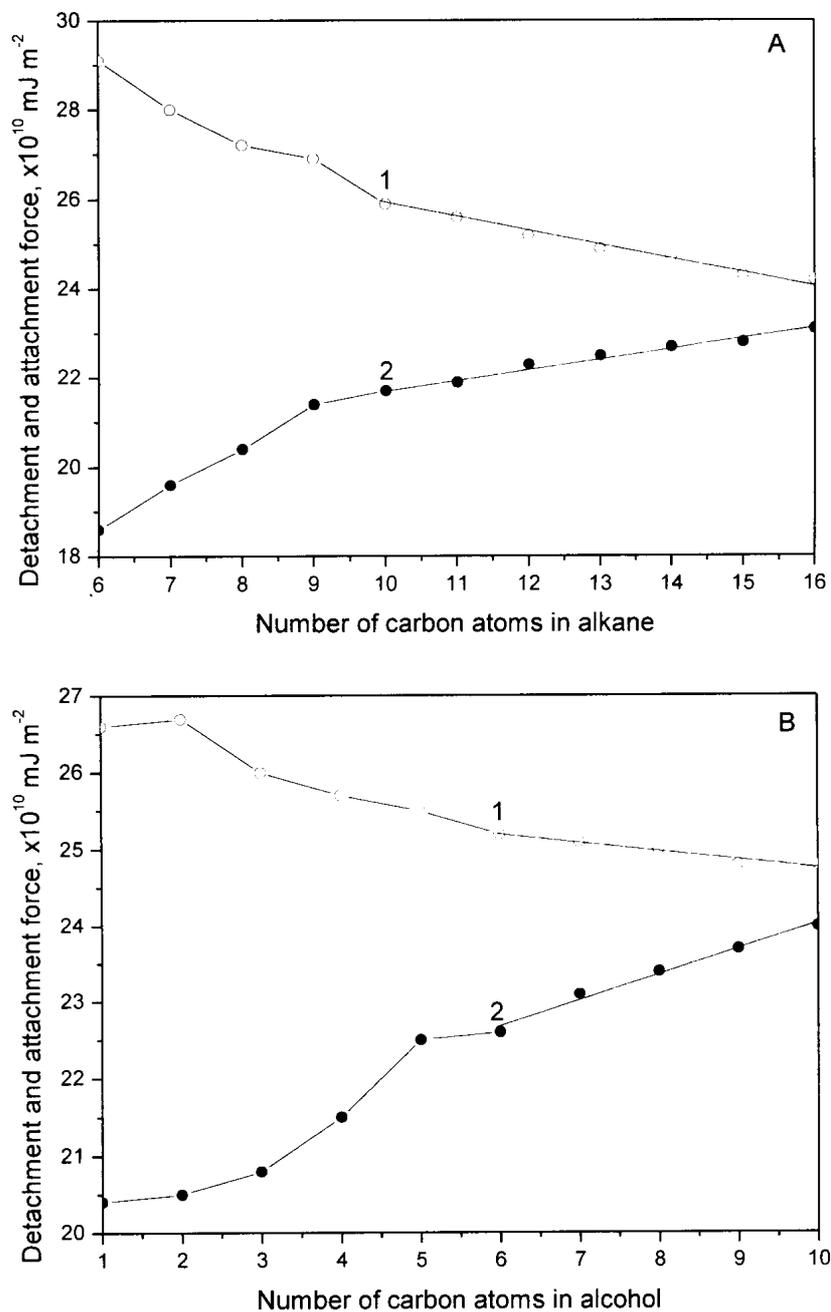


Fig. 2. The detachment (curve 1) and attachment (curve 2) forces as a function of the number of carbon atoms in molecule of alkanes (Fig. 2A) and alcohols (Fig. 2B)

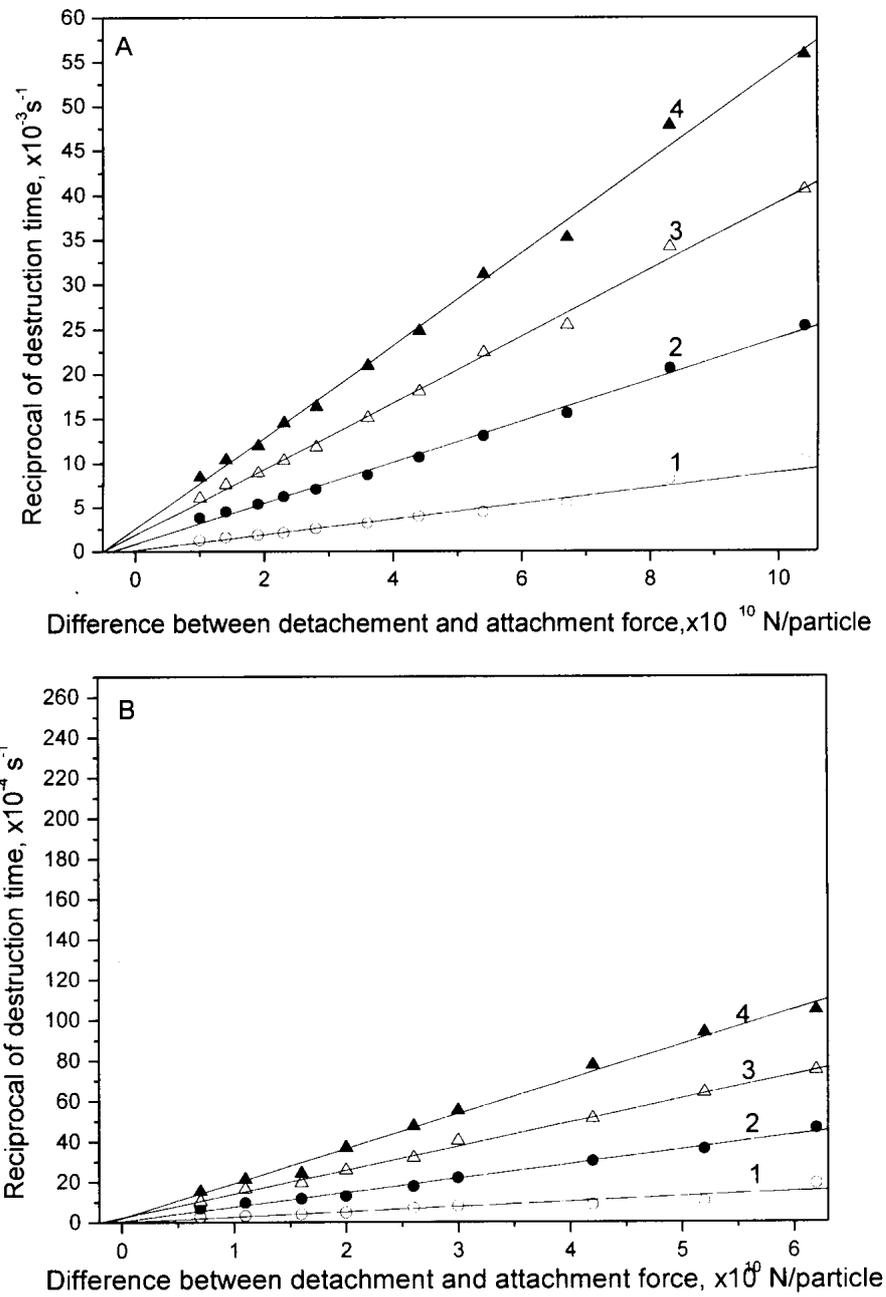


Fig. 3. Relationship of the reciprocal of the destruction time of coal sediment column structure as a function of the density differences between coal and alkanes (Fig. 3A), and coal and alcohols (Fig. 3B)

It is seen from the results presented in Fig. 3 that the curves would start from the beginning of the co-ordinate system if the values of  $\Delta F$  (Tab. II) were smaller by about  $0.4 \cdot 10^{-10}$  N/particle and  $0.13 \cdot 10^{-10}$  N/particle for alkanes and alcohols, respectively. To obtain these smaller values of  $\Delta F$ , the attachment force should be enhanced by  $0.4 \cdot 10^{-10}$  N/particle and  $0.15 \cdot 10^{-10}$  N/particle for alkanes and alcohols, respectively. Thus the attachment force for alkanes and alcohols is in the range from  $19.1 \cdot 10^{-10}$  N/m to  $23.6 \cdot 10^{-10}$  N/particle and from  $20.55 \cdot 10^{-10}$  N/particle to  $23.85 \cdot 10^{-10}$  N/particle, respectively. Then the values of the attachment force per unit of the perimeter length of the contact plane were calculated and listed in Tab. II. As it is seen the value of the attachment force is bigger by 1 mN/m than the work of cohesion of alcohols. It is evident that the detachment of coal particles from the sediment column occurred by disruption of the liquid film present between them. The attachment force between coal particles in alkanes and alcohols is a little bigger than the work of cohesion of the liquid. It means that the origin of the attachment force is the work of cohesion of the liquid and work of adhesion coal-liquid.

## CONCLUSION

The presented analysis and discussion of the results of the detachment experiments has clearly shown that detachment of coal particle from one another in the studied liquids occurs by disruption of the liquid film present between them.

The perimeter of the contact plane between two coal particles decreases with increasing length of the hydrocarbon chain of alkanes and alcohols. Increase of the destruction time of the sediment column structure of coal particles with increasing length of the hydrocarbon chain of the studied liquids results on the one hand from decrease of the detachment force of coal particle and from one another and on other from an increase of the attachment force between them.

The values of the attachment force is determined by the cohesion work of alkane or alcohol and by the adhesion work of coal – studied liquid.

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Wykorzystując opublikowane wartości czasu destrukcji struktury słupka sedymentu w rurce szklanej dla frakcji ziaren węgla o średniej średnicy  $1.5 \times 10^{-4}$ m,  $2.5 \times 10^{-4}$ m,  $3.5 \times 10^{-4}$ m i  $4.5 \times 10^{-4}$ m, w węglowodorach od heksanu do heksadekanu i alkoholach od metanolu do dekanolu, przeprowadzono badania nad korelacją pomiędzy czasem destrukcji a właściwościami objętościowymi badanych cieczy i węgla oraz międzyfazowymi ciecz-powietrze, węgiel-powietrze i węgiel-ciecz. Na podstawie przeprowadzonych badań stwierdzono, że czas destrukcji rośnie ze wzrostem długości łańcucha węglowodorowego alkanów i alkoholi a maleje ze wzrostem średniej średnicy ziaren węgla. Zmiany czasu destrukcji wynikają z różnicy pomiędzy siłami odrywającymi ziarno węgla od ziarna węgla a siłami adhezyjnymi (zlepiania), które odpowiednio zależą od oddziaływań grawitacyjnych i międzyfazowych. Obliczone siły odrywające, przy założeniu, że ziarna węgla są kulkami, maleją ze wzrostem długości łańcucha węglowodorowego badanych cieczy.

Dla obu badanych szeregów homologicznych stwierdzono liniową zależność pomiędzy odwrotnością czasu destrukcji słupka sedymentu i średnią średnicą badanych frakcji ziaren węgla, pracą kohezji alkanów i alkoholi, ich gęstością, różnicą gęstości węgla i badanych cieczy oraz swobodną energią oddziaływań w przeliczeniu na jedną cząsteczkę cieczy.

Prostoliniowe zależności pozwoliły na wyznaczenie tzw. „krytycznych wartości” takich parametrów jak: średnica ziaren, praca kohezji, gęstość, różnica gęstości i swobodna energia oddziaływań dla nieskończonego czasu destrukcji ( $1/t=0$ ). Dla układów o krytycznych wartościach wymienionych parametrów siły odrywania równe są siłom zlepiania. Biorąc to pod uwagę obliczono promień płaszczyzny kontaktu oraz wielkość sił zlepiania pomiędzy ziarnami węgla w badanych cieczach. Przeprowadzone obliczenia wykazały, że siły zlepiania pomiędzy ziarnami węgla są nieco wyższe od pracy kohezji badanej cieczy. Wynika z tego, że o wielkości sił zlepiania pomiędzy ziarnami węgla w badanych cieczach decyduje nie tylko wielkość pracy kohezji danej cieczy ale również wielkość pracy adhezji węgiel-badana ciecz. Ponieważ praca adhezji jest większa od pracy kohezji, zatem niszczenie struktury słupka sedymentu ziaren węgla zachodzi w wyniku przzerwania ciekłego filmu pomiędzy dwoma ziarnami węgla.