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Floatability of coals as a function of surface activity of the alcohols

Key words

Coal, flotation, surface tension, surface activity, alcohols

Abstract

It is a common practice in flotation to compare the action of various reagents on the basis of results of experiments carried out at several concentrations or amounts of reagents, identical for each reagent used. The same concentrations do not mean, however, the same surface coverages or the same dispersion of gas bubbles in the flotation cell. In this paper, results of flotation of various coals were analysed as a function of concentration and surface activity of aliphatic alcohols. Coal slimes from the Halemba, Rydułtowy, and Pokój Mines were floated. The aliphatic alcohols used as collecting/frothing agents were n-butanol and n-pentanol, and n-hexanol. It was found that the concentrate yields and ash content in tailings increase with the concentration of these alcohols. Also, at the same bulk concentrations, the longer the hydrocarbon chain of the alcohol molecule, the better the flotation results. The increase in floatability of coals with the length of the hydrocarbon chain in the alcohol molecule is associated with a simultaneous increase in surface activity of the homologous series of alcohols. When the processes are compared at the same surface activity (the same surface pressure), the concentrate yields are practically independent of the alcohol used. This shows that the action of aliphatic alcohols in flotation consisted mainly in enlarging the solution-gas interface, and their collecting properties in respect to coal slimes studied were very similar.

Introduction

The result of flotation depends highly on surface properties of the grains floated. To modify the grain surface and to increase aeration of the flotation pulp, special reagents are added, collectors and frothers. In coal flotation the grain surface is naturally hydrophobic, but the degree of hydrophobicity depends on the rank of coal. Also, coal surface hydrophobicity changes

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(lowers) as a result of surface oxidation (Stachurski et. al. 1980; Małysa 1981; Małysa, Stachurski 1982; Małysa, Stachurski 1988; Sablik 1998). Flotation reagents are added to obtain optimal flotation conditions. There are no generally accepted physicochemical properties to be used as a basis for comparing flotation reagents. Comparison is done by making flotation experiments at several concentrations or amounts (expressed in g per Mg) of employed reagents employed, identical for all the reagents employed (Stachurski, Małysa 1980; Małysa 1981; Małysa et. al. 1987; Małysa et. al. 1994). Molarity is a bulk quantity and thus the same bulk concentrations of various reagents do not correspond to the same surface coverage or the same dispersion of air bubbles in the flotation cell. That is why comparing flotation results on the basis of bulk quantities is not the best idea. A more reasonable approach seems to be a comparison of the effect of various reagents on flotation results on the basis of properties characterising the interface, such as surface tension, foaming index, etc., (Małysa et. al. 1987).

This paper presents the results of studies on the effect of changes in surface activity of three alcohol homologs on the results of flotation of medium-rank coals. For this purpose, surface tensions of the alcohol solutions under investigation were determined and the dependence of flotation results on the surface tension was analysed.

1. Subject and method of investigation

Three alcohols of the homologous series of aliphatic alcohols: n-butanol (C_4H_9OH), n-pentanol ($C_5H_{11}OH$), and n-hexanol ($C_6H_{13}OH$), of the aliphatic alcohol homologous series were used in the experiments. The alcohols were used in quantities permitting their solubility in water. Surface tension of their solutions was measured by the stalágmometric (drop weight) method (Adamson 1963). The mass of drops was calculated as the average of measurements of 5 drops. The surface tension measurement was repeated at least three times for each solution, and the average value was calculated.

The coal slimes studied were taken from the feed directed to sedimentation ponds and originated from the Halemba (type 34), Rydułtowy (type 34), and Pokój (type 33) Mines. The tests were performed in alcohol solutions of different concentrations. The slimes differed in ash and sulphur contents, and in grain size. Flotation of the coals was performed in a 1 dm^3 laboratory flotation cell at room temperature. The density of the flotation pulp was 80 g/dm^3 . Fractional flotation was performed. The results of the coal slime flotation were analysed in terms of their dependence on surface tension of the alcohol solutions. Surface pressure of a solution is equal to the difference of surface tensions of water and the solution of a given concentration ($\Pi = \sigma_0 - \sigma$).

2. Discussion of the results

The values of surface tensions of the alcohol solutions of different concentrations are given in Table 1 and in Fig. 1.

These data show that aqueous solutions of the studied aliphatic alcohols have lower surface tensions than pure water. Alcohol molecules tend to concentrate at the liquid-gas interface which

TABLE I

Surface tensions of solutions of aliphatic alcohols: n-butanol, n-pentanol and n-hexanol

TABELA I

Napięcia powierzchniowe roztworów alkoholi alifatycznych: n-butanolu, n-pentanolu i n-heksanolu

c [mole/dm ³]	C ₄ H ₉ OH		C ₅ H ₁₁ OH		C ₆ H ₁₃ OH	
	σ [mN/m]	Π [mN/m]	σ [mN/m]	Π [mN/m]	σ [mN/m]	Π [mN/m]
0	72.74	0.00	72.74	0.00	72.74	0.00
2 · 10 ⁻⁴	72.74	0.00	72.64	0.10	72.35	0.39
2.5 · 10 ⁻⁴	72.70	0.04	72.41	0.33	72.25	0.49
5 · 10 ⁻⁴	72.66	0.08	72.39	0.35	71.69	1.05
10 · 10 ⁻⁴	72.57	0.17	72.08	0.66	70.78	1.96
20 · 10 ⁻⁴	72.42	0.32	71.43	1.32	68.67	4.08
25 · 10 ⁻⁴	72.37	0.37	71.29	1.45	67.08	5.66
50 · 10 ⁻⁴	71.97	0.77	69.43	3.31	60.89	11.85

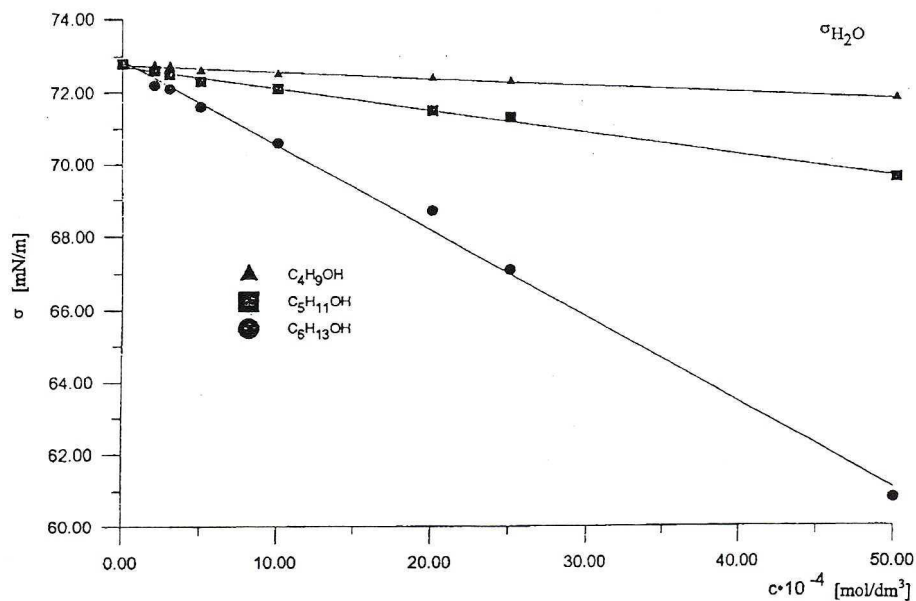


Fig. 1. Surface tensions of the alcohol solutions as a function of their concentration

Rys. 1. Napięcia powierzchniowe roztworów alkoholi w zależności od ich stężenia

results in the observed lowering of surface tension. The higher the concentration of the alcohol solutions, the lower their surface tensions (Fig. 1). For example, for a $5 \cdot 10^{-4}$ [mole/dm³] n-butanol solution, the surface tension is 72.66 [mN/m], whereas for a $5 \cdot 10^{-5}$ [mole/dm³] solution, the surface tension is 71.97 [mN/m]. The surface tension of water, as measured at 20°C, was 72.74 [mN/m], hence the values of surface tension lowering, that is surface pressures, of the above mentioned n-butanol solutions were 0.08 [mN/m] and 0.77 [mN/m], respectively (Tab. 1). Similarly, for the same concentrations of n-hexanol, the surface tensions are 71.69 [mN/m] and 60.98 [mN/m], and the corresponding values of surface tension lowering are 1.05 [mN/m] and 11.85 [mN/m].

The comparison of the surface activity changes with the length of the hydrocarbon chain of the alcohol showed that the longer the chain length, the lower the surface tensions. This result is consistent with Traube's rule which says that in order to produce the same surface tension with a homolog having one more -CH₂ group, three times lower concentration is needed (Traube, 1891). For example, the surface tension of 72.00 [mN/m] was obtained for alcohols C₄H₉OH, C₅H₁₁OH, and C₆H₁₃OH at concentrations of $3.7 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$, and $0.4 \cdot 10^{-3}$ [mole/dm³] (Fig. 1). As can be seen, in order to obtain the same value of surface tension, one has to use three times lower concentration of n-hexanol than that of n-pentanol, and three times lower concentration of n-pentanol than that of n-butanol. The increase in concentration increases adsorption of alcohols on the liquid-gas interface, which lowers surface tensions of these solutions.

Langmuir presented an illustrative interpretation of Traube's rule (Langmuir 1947). The work *W* needed to transfer 1 mole of the solute from the bulk of the solution to the surface is:

$$W = RT \ln c_s/c = RT(\ln \Gamma/(\tau c)),$$

where:

- c_s — surface concentration, equal Γ [mole/cm³],
- Γ — surface excess [mole/cm²],
- τ — surface area thickness [Å]
- R — universal gas constant [kJ/mole·K],
- T — temperature [K].

For two substances with chain lengths of *n* and *n*-1, the difference in the work *W* can be expressed as:

$$W_n - W_{n-1} = RT \ln [\Gamma_n c_{n-1}/(\Gamma_{n-1} c_n)].$$

From Traube's rule it follows that if $c_{n-1}/c_n = 3$, then $\sigma_n = \sigma_{n-1}$ and it can be assumed that surface concentrations of both substances are the same, that is $\Gamma_{n-1} = \Gamma_n$. If this is true, we obtain the following relationship:

$$W_n - W_{n-1} = RT \ln 3 = 640 \text{ [cal/mole]}.$$

The value of 640 [cal/mole] can be considered as the work needed to transfer one $-\text{CH}_2$ group from the bulk of solution to the surface area. As the value of 640 [cal/mole] apparently does not depend on the length of the hydrocarbon chain length, it can be assumed that all $-\text{CH}_2$ groups are situated on the surface the same way.

To determine the effect of surface activity of alcohols on coal slime flotation results, flotation of coal was studied as a function of alcohol molar concentration. The alcohols were used in quantities ensuring solubility in water, thus eliminating problems with their emulsification. The studied slimes differed in ash content. The coal slime from the Halemba Mine contained about 17% ash, whereas the slimes from the Rydułtowy and Pokój Mines contained 27% and 36% ash, respectively. The coals from the Halemba and Rydułtowy Mines belong to type 34, and the coal from the Pokój Mine belongs to class 33. The results of flotation are illustrated only for the slime from the Pokój Mine (Fig. 2), showing the dependence of concentrate yield (γ), ash content in concentrate (ν) and tailings (β) on alcohol molar concentration. It can be seen that the concentrate yields and ash contents in the tailings after three-minute flotation increase with the

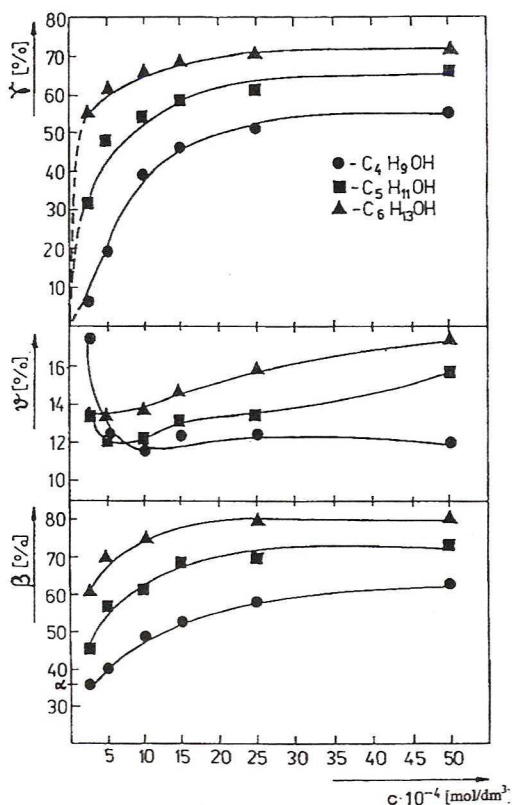


Fig. 2. Influence of the kind of alcohol and its concentration on flotation yields, contents of ash in the concentrates and tailings after 3 minutes flotation of coal from the "Pokój" Mine

Rys. 2. Wpływ stężenia i rodzaju alkoholu na wychody, zawartości popiołu w koncentratkach i odpadach po trzech minutach flotacji węgla kamiennego z kopalni „Pokój”

alcohol concentration. Also, the concentrate yields increase with the length of hydrocarbon chain in the alcohol molecule. For a given alcohol concentration, the lowest yields of concentrate and ash content in the tailings were noted for n-butanol, and the highest ones, for n-hexanol. Table 2 presents, for example, the yields of the studied coals at alcohol concentration of 10^{-3} [mole/dm³] after three-minute.

The observed increase in coal floatability with the increase in hydrocarbon chain length of the alcohol molecule can be explained by the simultaneous increase in the surface activity of the

TABLE 2

Yields of the concentrates for coals from "Halemba", "Rydułtowy" and "Pokój" Mines after three minutes of flotation in 10^{-3} mole/dm³ solutions of alcohols

TABELA 2

Wychody koncentratów węgla z Kopalni „Halemba”, „Rydułtowy” i „Pokój” po trzech minutach flotacji w roztworach alkoholi o stężeniu 10^{-3} mol/dm³

Alcohol	Halemba	Rydułtowy	Pokój
n-butanol	73	39	34
n-pentanol	85	54	60
n-hexanol	88	65	69

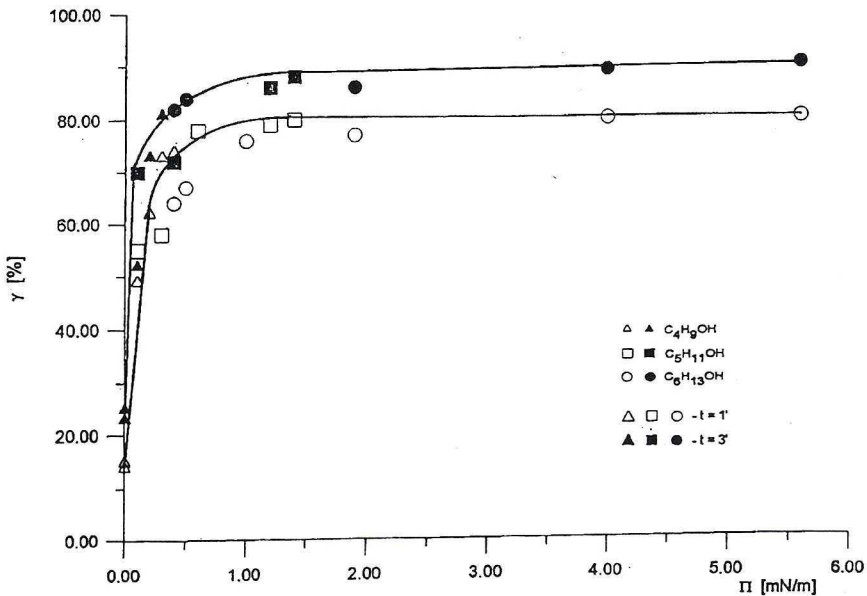


Fig. 3. Influence of the surface pressure of n-butanol, n-pentanol and n-hexanol solutions on yields of the coal concentrates from the "Halemba" Mine

Rys. 3. Wpływ ciśnienia powierzchniowego roztworów n-butanolu, n-pentanolu i n-heksanolu na wychody koncentratów węgla z kopalni „Halemba”

homologous series of alcohols. As already mentioned, the increase in the hydrocarbon chain of alcohols, in accordance with Traube's rule, in order to produce the same surface tension with a homolog having one more $-\text{CH}_2$ group, a three times lower concentration is needed than in the case of the lower homolog. The lowering of the surface tension of the solution is a quantity associated with alcohol adsorption on the liquid-gas interface. Also, the lowering of surface tension of a solution is associated with the level of gas dispersion, that is the gas bubble size in the flotation pulp. It can be assumed that for solutions of equal surface tensions the same air bubble size distribution is obtained in the flotation cell. This assumption means that alcohol solutions of equal surface tension, have the same degree of liquid-gas interface development.

To compare flotation results at equal surface activity of alcohols, the dependence of concentrate yield on the surface tension lowering (surface pressure $\Pi = \sigma_0 - \sigma$, where σ_0 — is the surface tension of water, and σ is the surface tension of the solution of a given concentration) was plotted (Figs. 3—5). This means that the same lowering of surface tension corresponds to various concentrations of different alcohols. The curves shown on these plots pertain to one-minute, and three-minute flotation. It was found that at the same lowering of in surface tension the yields of concentrates are similar, irrespective of the alcohol used (Figs. 3—5). For instance, for a surface tension of 0.4 [mN/m], the yields of concentrates are: 81—83% for the Halemba Mine, about 53% for the Rydułtowy Mine, and 49—51% for the Pokój Mine. The amount of surface tension lowering is associated with the degree of gas dispersion in the flotation pulp. The higher the gas dispersion degree, the more developed the liquid-gas interface and the higher the probability that

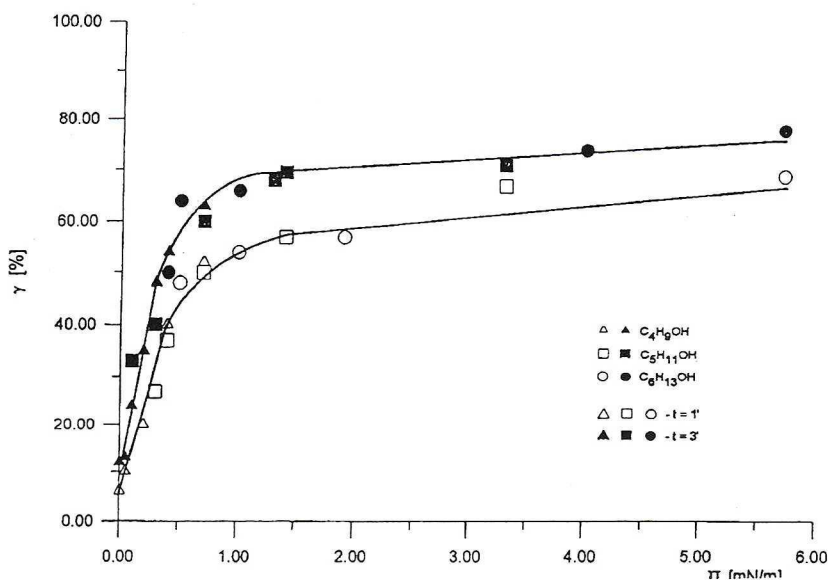


Fig. 4. Influence of the surface pressure of n-butanol, n-pentanol and n-hexanol solutions on yields of the coal concentrates from the "Rydułtowy" Mine

Rys. 4. Wpływ ciśnienia powierzchniowego roztworów n-butanolu, n-pentanolu i n-heksanolu na wychody koncentratów węgla z kopalni „Rydułtowy”

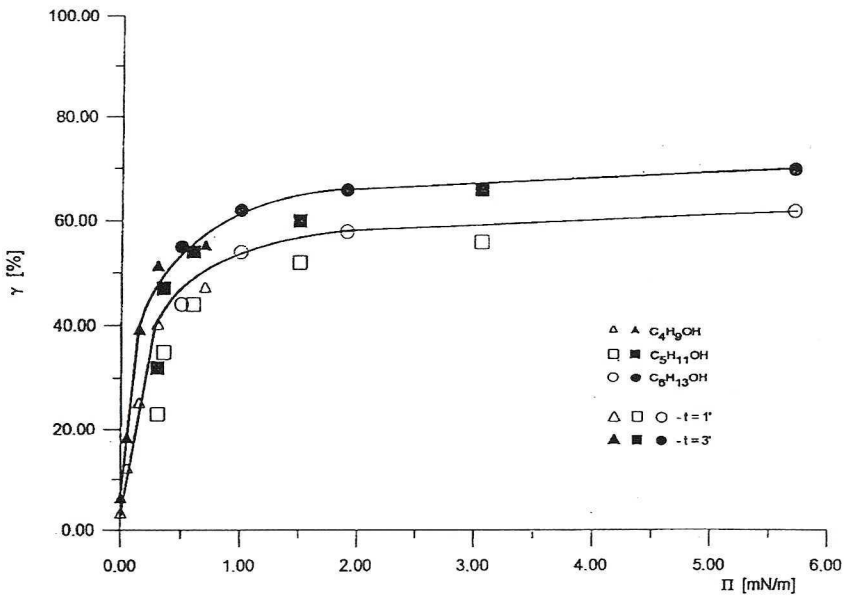


Fig. 5. Influence of the surface pressure of n-butanol, n-pentanol and n-hexanol solutions on yields of the coal concentrates from the "Pokój" Mine

Rys. 5. Wpływ ciśnienia powierzchniowego roztworów n-butanolu, n-pentanolu i n-heksanolu na wychody koncentratów węgla z kopalni „Pokój”

a coal grain would meet an air bubbles. The fact that for the studied alcohols, n-butanol and n-pentanol, and n-hexanol, the concentrate yields are the same at the same lowering of surface tension demonstrates that their action consists mainly in developing the liquid-gas interface, and their collecting properties in respect to coals are very similar.

Summary and conclusions

So far, the action of various reagents has been compared in flotation practice by carrying out experiments at several concentrations or amounts of reagents, identical for all reagents. The same amount or molarity of various reagents does not correspond to the same coverages or the same gas bubble dispersion in the flotation cell, and it is these factors that affect flotation results. That is why such a method of comparing flotation results does not seem to be the best one. That is why the objective of this study was to compare results of coal flotation in n-butanol and n-pentanol, and n-hexanol in respect to their surface activities.

The surface activity of aliphatic alcohols increases with the length of the hydrocarbon chain of the alcohol molecule. Of the alcohols tested, n-hexanol has the highest surface activity. It has the lowest surface tension in the whole range of concentrations studied. In order to produce the same decrease in surface activity, a three times lower concentration of

n-hexanol is needed than that of n-pentanol, and three times lower concentration of n-pentanol than that of n-butanol.

Coal flotation depends on the concentration and type of aliphatic alcohol used. The increase in alcohol concentration increases the concentrate yields and ash content in the tailings. At the same bulk concentration of alcohol, the flotation results were the better, the longer was the hydrocarbon chain the alcohol molecule. The increase in coal floatability with the hydrocarbon chain length in the alcohol molecule is associated with a simultaneous increase in surface activity of the homologous series of alcohols.

It has been found that at the same surface activity (the same lowering of surface tension) the yields of concentrates of the coals studied do not practically depend on the type of alcohol used. Hence, the action of aliphatic alcohols in flotation consists chiefly in increasing the gas-liquid interface, whereas their collecting properties in respect to coals are very similar.

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FLOTOWALNOŚĆ WĘGLI W FUNKCJI AKTYWNOŚCI POWIERZCHNIOWEJ STOSOWANYCH ALKOHOLI

Słowa kluczowe

Węgiel, flotacja, napięcie powierzchniowe, aktywność powierzchniowa, alkohole

Streszczenie

W praktyce flotacyjnej porównuje się działanie różnych odczynników robiąc doświadczenia dla kilku jednakowych ilości lub ich stężeń molowych. Temu samemu stężeniu molowemu nie odpowiada to samo pokrycie powierzchni i ta sama dyspersja pęcherzyków gazu w komorze. W pracy przeprowadzono analizę wyników flotacji węgla w funkcji stężenia i aktywności powierzchniowej alkoholi alifatycznych. Flotowano muły węglowe pochodzące z trzech różnych kopalń: „Halemba”, „Rydułtowy” i „Pokój”. Stosowano alkohole alifatyczne: n-butanol, n-pentanol i n-heksanol jako odczynniki zbierająco-pianotwórcze. Stwierdzono, że wraz ze wzrostem stężenia alkoholi rosną wychody koncentratów i zawartości popiołu w odpadach. Ponadto przy tym samym stężeniu objętościowym wyniki flotacji były tym lepsze, im dłuższy był łańcuch węglowodorowy w cząsteczce alkoholu. Wzrost flotowalności węgla wraz ze wzrostem długości łańcucha węglowodorowego w cząsteczce alkoholu związany jest z zachodzącym w tym samym kierunku wzrostem aktywności powierzchniowej w szeregu homologicznym alkoholi. Jeżeli porównanie wykona się przy tej samej aktywności powierzchniowej (przy tym samym ciśnieniu powierzchniowym), to wychody koncentratów badanych węgla są praktycznie niezależne od rodzaju użytego alkoholu. Wynika stąd, że działanie alkoholi alifatycznych w procesie flotacji polega głównie na rozwinięciu powierzchni międzyfazowej gaz-ciecz, a ich własności zbierające względem węgla są bardzo zbliżone.