The Effect of Propanol on the Contact Angle in the System Graphite/n-Alkane Film-Air Bubble-Solution

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Measurements of the contact angle were made in the system graphite/hydrocarbon film-air bubble-propanol aqueous solution. Hexane, decane and hexadecane films were tested in propanol solutions at concentration from 0 to 300 mg/dm³. The results obtained were compared with those calculated from the modified GGFY equation (Good-Girifalco-Fowkes-Young). On the basis of the studies and calculations carried out it has been found that polar and nonpolar liquids considerably change the wettability of high-energy hydrophobic graphite. This wettability depends on the thickness and nature of nonpolar liquid film on graphite surface and on the concentration of polar liquid solutions. It has also been suggested that, in the presence of polar liquid (propanol) at the interface of graphite/hydrocarbon film-solution, polar interactions appear between alcohol molecules adsorbed on the interface and water molecules.

INTRODUCTION

The effect of nonpolar and especially polar liquids on the wettability of solids with water is of significant importance, for example, in the flotation process of mineral enrichment. The effectiveness of this process depends on the interfacial properties of a three-phase system: solid-air-liquid. However, the possibility of formation of such a system depends on the nature and magnitude of interfacial interactions i.e. interfacial energy.

Due to the presence of a nonpolar liquid on the surface of a hydrophobic high-energy solid (sulphur, graphite, and the like), the interfacial free energies of solid-liquid and solid-air are changed. Accordingly, the stability of the system solid-air-liquid is also changed.

In such a system, the wetting process of water can well be explained on the basis of Young's equation, where the parameter determining the film pressure of nonpolar liquid was introduced. Polar liquids introduced into the three-phase system also change the interfacial free energies of the interfaces, but the nature and magnitude of these changes are different from those in the case of nonpolar liquids.

The studies have shown that the change of the interfacial free energy of hydrophobic solid-water interface takes place in solutions of a polar
liquid as a result of the polar interactions between the adsorbed and oriented molecules of the polar liquid and those of the bulk phase.

The magnitude of the polar interactions can be determined from the equation of Good-Girifalco-Powkes-Young (GGFY) as extended by the term of the interfacial polar interactions. These interactions are especially conspicuous in the concentration range from 0 to 300 mg/dm³ of the polar substance (alcohol) in water, i.e. the range sometimes encountered in the flotation process. In the flotation system, a polar and nonpolar liquid are sometimes used simultaneously and their joint effect on the stability of the three-phase system is more complex than their separate effects. There are relatively few experimental data and few theoretical papers in the literature concerning the simultaneous use of polar and nonpolar liquids in the wetting process of solids. For this reason measurements of the contact angle in the system graphite/n-alkane film-air-bubble-aqueous solution of propanol were carried out for the film of hexane, decane, and hexadecane, and at the concentration range of the solution from 0 to 300 mg/dm³ in water.

Theory

Introducing nonpolar and polar liquids into the system of solid-air bubble-water, the contact angle value of an air bubble captivated on the solid surface may be changed. This is likely to occur because of the film of nonpolar and polar liquids formed under the air bubble and behind it (by adsorption and the spreading process) and because of the change in the surface tension of water caused by these liquids.

The equilibrium state for the system graphite-air bubble-water in the presence of nonpolar (hydrocarbon) and polar (alcohol) liquids can be expressed by Young's equation:

\[ \gamma_{SI} - \gamma_{SL} - \pi e = \gamma_L \cos \theta \]

where:
- \( \gamma_{SI} \) is the surface free energy of the graphite covered with hydrocarbon film,
- \( \gamma_{SL} \) is the interfacial free energy of graphite/hydrocarbon film-aqueous alcohol solution,
- \( \gamma_L \) is the surface tension of alcohol solution/hydrocarbon film,
- \( \pi e \) is the magnitude of \( \gamma_{SI} \) reduction by adsorption of water and alcohol molecules on the surface graphite/hydrocarbon film,
- \( \theta \) is the contact angle measured through the liquid phase.

From Eq. (1) it follows that \( \theta \) is a function of many variables (\( \gamma_{SI}, \gamma_{SL}, \gamma_L, \pi e \)). It is possible to calculate \( \theta \) values from this equation, if the dependences between them are known. According to the theory of interfacial interactions it can be written:

\[ \gamma_{SL} = \gamma_{SI} + \gamma_L - f(\gamma_{SI}, \gamma_L) \]

where \( f(\gamma_{SI}, \gamma_L) \) determines the dispersion and polar interfacial interactions at the interface graphite/hydrocarbon film-aqueous alcohol solution.

Polar interfacial interactions may occur at this interface because of the adsorption and proper orientation of alcohol molecules at the surface graphite/hydrocarbon film.

Many methods for calculating interfacial interactions at solid-liquid interface are known. Busscher et al. have pointed out that the geometric...
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mean of dispersion and polar interfacial interactions, which may be controversial,20,27-29 gives good results when used for calculations of solid-aqueous propanol solution interfacial free energy.

Taking this into account and assuming that \( \gamma_S = \gamma_S - \pi^n \) \( (\gamma_S \approx \gamma_S^d) \),

\( \pi^n \approx 0 \) (for \( \gamma_S \leq \gamma_L \))14 and that \( \gamma_L \approx \gamma_L^d \) (for very stable films on high energy solid surface\(^{5,31,32} \)), e.g. graphite\(^{14,30} \) from Eq. (1) we obtain:

\[
\gamma_L \cos \Theta = -\gamma_L + 2 \sqrt{(\gamma_L^d - \pi) \gamma_L^d} + \gamma_{SW}^p \tag{3}
\]

where: \( \gamma_L \) is the solution surface tension, \( \gamma_L^d \) is the dispersion component of solution surface free energy of graphite \( (\gamma_L, \pi) \) is the hydrocarbon film pressure and \( \gamma_{SW}^p \) is the polar term of interfacial interactions at graphite/hydrocarbon film-aqueous alcohol solution, which is similar to the geometric mean of polar interfacial interactions between the graphite/hydrocarbon film surface and the solution surface.

The studies on the wettability of hydrophobic solids in the presence of polar liquids suggest that maximal values of \( J_{SL}^p \) at the interface hydrophobic solid-aqueous alcohol solution are approximately equal to \( 2 \sqrt{\gamma_L^d \gamma_{SW}^p} \) (where \( \gamma_L^d \) and \( \gamma_{SW}^p \) are polar components of the solution surface tension of alcohol and water, respectively).16 The \( J_{SL}^p \) values correspond to the concentration of 300 mg/dm\(^3\) of alcohol in water.

Assuming that, because of the adsorption of the alcohol molecules on the surface of graphite/n-alkane film, polar interactions may appear at the interface whose value is equal to \( x_{AI} \gamma_L \) \( (x_{AI} \gamma_L \) is a factor whose value may change from 0 to 1). Hence, the possible polar interactions with water molecules may occur and Eq. (3) may be rewritten in the following form:

\[
\gamma_L \cos \Theta = -\gamma_L + 2 \sqrt{(\gamma_L^d - \pi) \gamma_L^d} + 2 \sqrt{x_{AI} \gamma_L^d \gamma_{SW}^p} \tag{4}
\]

Eq. (4) takes into account the influence of nonpolar and polar liquids on the wettability of hydrophobic solids \( (\Theta = f(n, c)) \), and it is not excluded that according to Vincent's theory\(^{33} \) the equality of \( 2 \sqrt{x_{AI} \gamma_L^d \gamma_{SW}^p} = 2 N_{AI} \gamma_L \) may take place, where \( N_{AI} \) is the molar fraction of alcohol in the interfacial region of graphite/n-alkane film-aqueous solution of alcohol.

However, this is difficult to verify, because it is difficult to determine the alcohol molecules adsorption on the surface of the graphite/n-alkane film.

On the basis of Eq. (4) one may analyze the change of \( \Theta \) values as a function of the hydrocarbon film pressure on graphite surface for \( x_{AI} = \text{const.} \) and changes of \( \Theta \) values as a function of aqueous alcohol solution concentration for \( \pi = \text{const.} \).

In this paper the changes of \( \Theta \) values as a function \( c \) for \( \pi = W_I \) and \( \pi = W_A \) (where \( W_I \) and \( W_A \) are the work of immersional wetting and adhesional wetting, respectively) are presented (see Results and Discussion). \( W_I \) and \( W_A \) values were calculated from the following equations:\(^{14,34} \)

\[
W_I = \gamma_S - \gamma_{SH} = 2 \sqrt{\gamma_S^d \gamma_{WH}^d} - \gamma_H \tag{5}
\]

\[
W_A = \gamma_S + \gamma_B - \gamma_{SB} = 2 \sqrt{\gamma_S^d \gamma_{BH}^d} \tag{6}
\]
where $\gamma_{SH}$ is the interfacial free energy of graphite-hydrocarbon, $\gamma_H$ is the surface hydrocarbon tension and $\gamma_{Hd}$ is the dispersion component of $\gamma_H$ \( \gamma_{TH} = \gamma_{TH}^{(S)} \approx \gamma_{TH}^{(Sd)} \approx \gamma_{TH}^{(Hd)} \).14,30

EXPERIMENTAL

Measurements of the contact angle in the system graphite/dydrocarbon film-air bubble-aqueous propanol solution were made by the method of captive air bubble using a microscope-goniometer system at magnification $\times 25$. For these measurements polished $1 \times 1$ cm graphite plates were used (the preparation of such plates was described elsewhere),14 on which the tested nonpolar liquid ($n$-alkane) was deposited in excess. After immersing the graphite plate wetted with hydrocarbon in propanol solution of an appropriate concentration (in the range from 0 to 300 mg/dm$^3$) a large air bubble was contacted with its surface, and, at a distance of about 2 mm from it, a small bubble ($1-2 \mu$) was also settled.

After about a 30 min. equilibration, the contact angle was measured for the small bubble and both air bubbles were removed. Then another small air bubble was contacted with graphite surface and after measuring the contact angle (after about 5 min.) it was removed. The above procedure was repeated until the contact angle value for the given system was established. All measurements were made at $20 \pm 0.1^\circ$C and the error was $\pm 1^\circ$.

RESULTS AND DISCUSSION

The values of the contact angles obtained from the measurements for the system graphite/$n$-alkane film-air bubble-aqueous propanol solution decreased for all propanol solution concentrations ($c$) used when the number of the contacting air bubbles ($n$) increased, which can be seen in Figure 1 (curves 1—6). In Figure 1, as an example, the relationship of $\theta$ as a function of the number of air bubbles contacted with graphite surface wetted respectively with: hexane (curve 1 — at a concentration of 20 mg/dm$^3$ of propanol in water, curve 2 — at a concentration of 300 mg/dm$^3$ of propanol in water), decane (curve 3 and 4 — similarly as for hexane) and hexadecane (curve 5 and 6 — similarly as for hexane).
of \( n \) is plotted for \( c = 20 \text{ mg/dm}^2 \) (curves 1, 3, 5) and \( c = 300 \text{ mg/dm}^2 \) (curves 2, 4, 6). Curves 1, 2 were obtained for hexane, curves 3, 4 for decane and curves 5, 6 for hexadecane. From Figure 1 it can also be seen that the contact angle as a function of \( n \) is \( c \) characterized by a drop in \( \Theta \) value at the proper number of air bubbles detached from graphite/\( n \)-alkane film surface. This number is greater for long-chain hydrocarbons (for example for hexane at 10—11 and for hexadecane at 24—37 detached bubbles).

Moreover, the drop of \( \Theta \) value for the given \( n \)-alkane, but at two different concentrations of propanol, occurs at a smaller number of \( n \) when the concentration of propanol is higher. The changes of \( \Theta \) values presented in Figure 1, which are a function of \( n \), may result from a decrease of \( n \)-alkane film thickness (decreases of the film pressure \( \pi \) on graphite surface caused by detaching air bubbles from it).\(^5,6,8\) The decrease of the film thickness may be considered as a result of the »reswelling« of \( n \)-alkane to the three-phase contact line,\(^3,5,6\) spreading of \( n \)-alkane over the air bubble surface,\(^13,35\) and partial evaporation of \( n \)-alkane into the air bubble (particularly for \( n \)-alkane having a remarkable vapour pressure at the measuring temperature).

It is difficult to explain the relationship of \( \Theta \) vs. \( c \) presented in Figure 1 and to estimate the film pressure \( \pi \) range connected with the changes of \( \Theta \) values.

The studies of \( n \)-alkane film properties on sulphur surface, for which surface free energy is similar in magnitude to that of graphite,\(^14,30,37,38\) by zeta-potential measurements have resulted in the conclusion that maximal thickness of a stable \( n \)-heptane film is such that the film pressure \( \pi \) corresponds to \( W_A \).\(^8\) Hence, it is assumed here that the maximal film pressure of hexane, decane and hexadecane on graphite surface, independently of the aqueous propanol solution concentration, is equal to the work of adhesion wetting process for these hydrocarbons in air, and its value has been calculated from Eq. (6). In the calculations the following values were used: \( \gamma_{\alpha}\perp = 122 \text{ mJ/m}^2,14\) and \( \gamma_{\alpha\perp} \) for hexane, decane and hexadecane equal to 18.49, 23.90 and 26.35 mJ/m\(^2\),\(^38\) respectively. Inserting the values of \( W_A \) into Eq. (4) \( \Theta \) values for different \( c \) were calculated and are presented in Figure 2 as a function \( \Theta \) vs. \( c \) (dashed lines).

In the calculations of \( \Theta \) from Eq. (4) it was assumed that the \( n \)-alkane film was thick and homogeneous, thus overshadowing a possible polar interfacial interaction between the functional groups which may exist on the graphite surface and water molecules.\(^38,46\) It was also assumed that the values of \( x_{\alpha\perp} \) were proportional to \( c \) (we assumed that the range of \( c \) from 0 to 300 mg/dm\(^2\) corresponded to the change of \( x_{\alpha\perp} \) from 0 to 1). The following values were used for the calculations: \( \gamma_{\alpha\perp} = 3.07 \text{ mN/m},10\) and \( \gamma_{\alpha\perp} = 51 \text{ mN/m}.14\) The values of \( \gamma_{\alpha\perp} \) and \( \gamma_{\alpha\perp} \) were taken from a previous paper.\(^41\) The changes of \( \Theta \) values which were measured for the first captive air bubbles (for the system graphite/\( n \)-alkane film-air bubble-solution) as a function of propanol concentration in water are also presented in Figure 2 (solid lines—curves 1—3).

From Figure 2 one can see that the values measured (curves 1—3) and calculated from Eq. (4) (curves 1'—3') for all systems studied decrease when \( c \) increases.
Figure 2. Effect of propyl alcohol concentration in water on the wetting contact angle in the system graphite/n-alkane film-air bubble-solution. Curve 1, 2, 3 — the wetting contact angle values measured for the first air bubble (Figure 1) in the system graphite/n-alkane film-air bubble-solution respectively for hexane (curve 1), decane (curve 2) and hexadecane (curve 3), curve 1', 2', 3' — wetting contact angle values calculated from Eq. (4), if \( x = W_A \) and \( x_A \) changes from 0 to 1 respectively for hexane (curve 1') decane (curve 2') and hexadecane (curve 3').

Comparing the curves obtained from the measured values with the theoretical ones for hexane (curves 1—1'), decane (curves 2—2') and hexadecane (curves 3—3') it can be found that in the range of propanol concentration from 0 to 120 mg/dm\(^3\) the calculated \( \theta \) values are similar to those measured, and above the concentration of 120 mg/dm\(^3\) the calculated \( \theta \) values are smaller than those measured. Hence, it may be concluded that the above mentioned assumption dealing with the maximal n-alkane film pressure value equal to \( W_A \) in the system graphite/n-alkane film-air bubble-solution is completely correct for low concentrations.

The changes of \( \theta \) value as a function of the propanol concentration in water probably result from polar interactions between the adsorbed propanol molecules on graphite/n-alkane film surface and water molecules from the bulk phase. Taking into account the fact that the changes of \( \gamma_{lv}, \gamma_{lp}^d \) and \( \gamma_{lp}^p \) in the studied range of \( c \) are small, the contribution of polar interactions of
water molecules with graphite/n-alkane film surface may be recognized as constant. Hence, if the polar interactions could result only from the functional groups of graphite surface, the changes of \( \Theta \) values would practically not be observed in the range of \( c \) values from 0 to 300 mg/dm\(^3\).

Recognizing the fact that the n-alkane film pressure for \( n = 1 \) corresponds to the work of adhesional wetting \( (W_A) \), it may be taken that the changes of \( \Theta \) values presented in Figure 1 are connected with the changes of \( \pi \) from \( \pi = W_A \) to \( \pi = \pi_{\min} \), where \( \pi_{\min} \) value depends upon the kind of n-alkane and concentration of the solution.

From the previous studies\(^{44,45} \) it was observed that the relationship of the film pressure \( \pi \) and the amounts of the liquid adsorbed on the solid surface showed inflection points which may correspond to spreading, immersion and adhesion wetting processes, and hence to \( W_A \), \( W_1 \) and \( W_s \), respectively.

Therefore, it is assumed that the drop in \( \Theta \) values appearing on curves 1—6 presented in Figure 1 can be connected with n-alkane film pressure equal to the work of immersional wetting. Using the above values of \( \gamma_s^d \) and \( \gamma_w^d \), the film pressure values were calculated from Eq. (5) for hexane, decane and hexadecane. Next, the values of \( \Theta \) were calculated from Eq. (4), using the above values of \( \gamma_s^0 \), \( \gamma_r^d \), \( \gamma_r^d \), \( \gamma_w^d \) and \( x_A \), and \( \pi = W_A \). Thus calculated values of \( \Theta \) are presented in Figure 3 as a function of \( c \) (dashed-line-curves 1'—3'). This figure presents the \( \Theta \) values measured in the system graphite/n-alkane film-air bubble-solution as a function of the aqueous propanol solution concentration (solid-line-curves 1—3). These \( \Theta \) values concern the last value before the drop of \( \Theta \) shown in Figure 1.

From Figure 3 it can be seen that both the measured and calculated \( \Theta \) values decrease when the \( c \) values increase. Comparing the solid curves with the dashed ones (for the same hydrocarbon) it may be concluded that the calculated and measured \( \Theta \) values are consistent. This suggests that in accordance with our assumption the thickness of hydrocarbon films on graphite surface corresponds to the film pressure equal to the work of immersional wetting.

It is very characteristic that the equilibrium \( \Theta \) values (Figure 1), measured in the system of graphite/n-alkane film (hexane, decane and hexadecane) — air bubble-aqueous propanol solution, are close to those measured in the system of graphite-air bubble-aqueous propanol solution (for the same concentration of propanol solution), which can be seen in Figure 4. The obtained \( \Theta \) values for the first system are marked in Figure 4 by points, and those for the second system (studied earlier\(^{47,48} \)) by the dashed line.

From Figure 4 it appears that, like in Figures 2 and 3, the \( \Theta \) values decrease when the solution concentration increases. Unfortunately, for minimal \( \Theta \) values (see Figure 1) it cannot be shown (on the basis of Eq. (4)) to what hydrocarbon film pressure these values correspond, because it is difficult to assume that \( \pi e \approx 0 \) (see theory); therefore, we do not known whether \( \gamma_s^d \leq \gamma_r^d \) or not in this case.

It cannot be rejected that n-alkane film is non-continuous and that polar interactions between functional groups (if they exist on the graphite surface) and water molecules are likely to appear.
Figure 3. A similar relationship as in Figure 2 obtained for that number of air bubbles at which a change of $\theta$ value occurs (see Figure 1) (curve 1, 2, 3 — $\theta$ values measured respectively for hexane, decane, hexadecane, curves 1', 2', 3' — $\theta$ values calculated from Eq. (4) if $\pi = W$, and $x A_p$ changes from 0 and 1 respectively for hexane, decane and hexadecane).

Figure 4. Change of the wetting contact angle values (see Figure 1) determined in the system graphite/$n$-alkane film-air bubble-solution (circles: ○ — hexane, ● — decane, ● — hexadecane) and that of the wetting contact angle in the system graphite-air bubble-solution (dashed line) as a function of propanol concentration in water.
The theoretical and experimental data presented above indicate that nonpolar and polar liquids change the wettability of relatively high-energy hydrophobic graphite.

The wettability with water depends on the thickness and nature of the film of nonpolar liquid on graphite surface and on the concentration of polar liquid in water. In the presence of polar liquid at interface graphite/n-alkane film-solution polar interactions between polar liquid molecules (adsorbed on graphite/n-alkane film surface) and water molecules can appear. These interactions considerably decrease the values of the contact angle for the system graphite/n-alkane film-air bubble-aqueous propanol solution.

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SAZETAK
Učinak propanola na kontaktni kut u sustavu grafit- n-ugljikovodikov film-zračni mjehurić otopina
J. Janczuk

Mjeren je kontaktni kut u sustavu grafit- n-alkanski film-zračni mjehurić vodena otopina. Filmovi heksana, dekana i heksadekana su ispitani u propanoliskoj otopini koncentracije 0 do 300 mg/dm³. Nađeno je da polarne i nepolarne tekućine znatno mijenjaju sposobnost vlaženja hidrofobnog grafit a visoke energije. Kada je prisutna polarna tekućina na graničnoj plohi tada se javljaju polarni interakcije između molekula vode i molekula alkohola koje su adsorbirane na graničnoj plohi.