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Influence of N-alkanes on contact angle and flotability of quartz

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Measurements of time dependence of the contact angle were carried out for water drops on a quartz surface in the presence of saturated hydrocarbon vapour as well as on a quartz surface previously wetted with a hydrocarbon. The results obtained were compared with theoretically calculated values on the basis of the modified Young equation and the literature data for the surface free energy components of quartz covered with a monolayer water film. On the basis of the measurements and calculations it was found that the values of the contact angle in the studied systems depend on the kind and thickness of hydrocarbon film present on the quartz surface, as well as on the thickness of water film present on this surface. Changes of the contact angle with the hydrocarbon film thickness are characterized by the maximum and minimum values. This allows previously obtained results of the quartz flotation activity changes in the presence of the aliphatic hydrocarbon films to be explained.

1. Introduction

Lin and Metzer [1] have shown that the presence of aliphatic hydrocarbons improve the effectiveness of quartz flotation. However, covering the quartz surface with n-alkanes only, even up to a calculated monolayer does not cause a significant flotation of quartz [2].

Recovery of such samples does not exceed 10% [2], and small minima and maxima appear in the function of the surface coverage with the alkane. Heterogeneity of the quartz surface influences structure of the alkane film, which is not uniform. Clusters of water and n-alkane molecules can be expected on the surface [3]. On the other hand it seems to be possible that alkane film forms not only on the clean surface but also on a monolayer water film [4, 5]. The presence of n-alkane film influences the dispersion and non-dispersion intermolecular interactions and thus the surface free energy of quartz. In consequence, conditions for air bubble adhesion to a grain in flotation process are also somewhat changed. Among others, a parameter for the adhesion strength determination is the stability of the quartz-air bubble-water system as measured by the detachment force [6].

Studies on the stability of this system have shown that in the same range of film thickness only one maximum appears on the disruption force – n-alkane film thickness curve, contrary to flotability [2, 6]. A close relationship exists between the stability of the three-phase system and the wetting contact angle value, thus measurements of the angle can be of assistance in explaining the observed disagreement of various parameters which describe the flotation process.

Thus, it seemed interesting to test the contact angle changes as a function of n-alkane film thickness on the quartz surface. For this purpose contact angles were measured in quartz–water drop–air (saturated alkane vapour), and quartz wetted with the alkane–water drop–air systems. Theoretical analyses for the equilibrium state reached in the studied systems have been done based on the contact angles and zeta potentials [2]. This was considered in aspects of the flotation activity of quartz.

2. Experimental techniques

For contact angle measurements 1 × 1 cm quartz plates were employed. The plates were obtained from quartz glass consisting of 99.99% SiO_2. They possessed a very smooth surface.

To remove possible surface contaminations the plates were treated with chromic mixture, then boiled three times in HCl (1 : 1), washed with doubly distilled water, boiled three times in doubly distilled water and cleaned in an ultrasonic bath for 20 min. Then they were dried and stored in a desiccator filled with molecular sieve (4A + 5A).

To measure the contact angle the plate was placed in a thermostated chamber filled with saturated vapour of n-heptane (a vessel with n-heptane was earlier placed inside the chamber) and immediately a water drop of 2 mm^3 volume was put on the surface, and contact angle was read on the left and right sides of the drop using a goniometer–telescope system with 25 × magnification. Then the chamber was "dried" with the molecular sieve (4A + 5A), again filled with n-heptane saturated vapour and a new quartz plate was placed inside it. This time, however, the water drop was put on the plate after it had been exposed for 5 min to the n-heptane vapour. The same procedure

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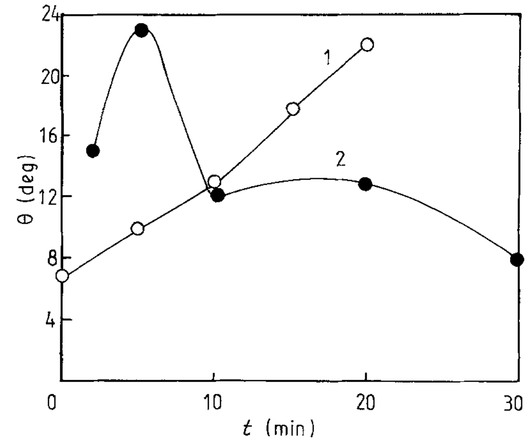

Figure 1 Relationship between the contact angle of water drop θ on the quartz surface and contact time, t. Curve 1: wetted by n-heptane quartz plate then dried by molecular sieve. Curve 2: "dry" quartz plate with n-heptane vapour.

was then repeated and, the plates were kept for 10, 20 and 30 min in the heptane vapour, before the water drop was introduced.

In the other series of experiments the quartz plates taken from the desiccator were dipped for a moment into n-heptane and placed in the measuring chamber, where molecular sieves (4A + 5A) were also placed. Then the water drop was introduced, first immediately, and then after 5, 10, 15, and 20 min, each time on a new quartz plate.

Analogical experiments were done using n-decane. All the measurements were conducted at $20 \pm 0.1\,^{\circ}\mathrm{C}$, and the contact angle experimental error was $\pm 1^{\circ}$.

3. Results and discussion

Contact angles measured in the above experiments are shown in Figs 1 and 2 as a function of contact time with saturated n-alkane vapour of "dry" plates (curves 2) or the "drying time" of wetted with n-alkanes plates (curves 1). From Fig. 1 it is seen that for quartz plates wetted with n-heptane contact angles increase monotonically as a function of time reaching 22° after 20 min. Quite different changes have been observed for "dry" quartz plates in contact with n-heptane vapour (curve 2). Here, a distinct maximum appeared after 5 min and a broad maximum after 20 min. In this case the highest contact angle value also reaches 22°.

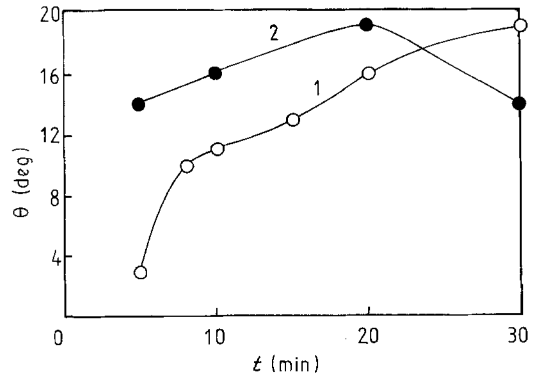

Figure 2 Relationship between the contact angle of water drop θ on quartz surface and a contact time (t). Curve 1: wetted by n-decane quartz plate then dried by molecular sieve. Curve 2: "dry" quartz plate with n-decane vapour.

In the system with n-decane presence, contact angles change in a somewhat different way (Fig. 2). Here, there is only a maximum after 20 min for "dry" quartz plate (curve 2) and the contact angles increase linearly up to this time of contact. The highest value of θ for decane is smaller by 4° than that for heptane.

An explanation for the observed changes of θ can be given based on a modified Young equation which can be written as follows

$$\gamma_{\mathrm{sf}_1} - \gamma_{\mathrm{sfw}} = \gamma'_{\mathrm{W}} \cos\theta \qquad (1)$$

where γ_{sf_1} is the surface free energy of quartz surface covered with hydrocarbon, or mixed hydrocarbon and water film behind the drop, γ_{sf} the surface free energy of quartz covered with hydrocarbon film but present only under the water drop, γ_{sfw} the interfacial free energy of quartz–hydrocarbon–water, γ'_{W} the surface tension of water changed by the presence of the hydrocarbon film, and the contact angle.

Assuming that

$$\gamma_{\mathrm{sf}} = (\gamma_{\mathrm{S}}^{\mathrm{d}} - \pi_1) + (\gamma_{\mathrm{S}}^{\mathrm{n}} - \pi_2) \qquad (2)$$

and

$$\gamma_{\mathrm{sf}_1} = \gamma_{\mathrm{sf}} - \pi \qquad (3)$$

and expressing γ_{sfw} as a geometric mean of dispersion and non-dispersion interfacial interactions [7–9], for $\gamma'_{\mathrm{W}} \approx \gamma_{\mathrm{W}}$, one obtains

$$\begin{aligned}\gamma_{\mathrm{W}} \cos\theta &= -\gamma_{\mathrm{W}} + 2[(\gamma_{\mathrm{S}}^{\mathrm{d}} - \pi_1)\gamma_{\mathrm{W}}^{\mathrm{d}}]^{1/2} \\ &\quad + 2[(\gamma_{\mathrm{S}}^{\mathrm{n}} - \pi_2)\gamma_{\mathrm{W}}^{\mathrm{n}}]^{1/2} - \pi \qquad (4)\end{aligned}$$

where $\gamma_{\mathrm{S}}^{\mathrm{d}}$ is the dispersion component of the surface free energy of quartz, $\gamma_{\mathrm{S}}^{\mathrm{n}}$ the non-dispersion component of the surface free energy of quartz, $\gamma_{\mathrm{W}}^{\mathrm{d}}$, $\gamma_{\mathrm{W}}^{\mathrm{n}}$ the dispersion and non-dispersion components of the surface tension of water, respectively π the difference between surface free energy of quartz covered with the films behind and under the water drop, π_1 the decrease of the dispersion component of the surface free energy of quartz (γ_{S}) by the hydrocarbon film and π_2 the decrease of the non-dispersion component of the surface free of quartz by hydrocarbon film.

From Equation 4 it is possible to analyse the contact angle θ changes as a function of the hydrocarbon film thickness which influences π, π_1 and π_2 values. However, the values of $\gamma_{\mathrm{S}}^{\mathrm{d}}$, $\gamma_{\mathrm{S}}^{\mathrm{n}}$, γ_{W}, $\gamma_{\mathrm{W}}^{\mathrm{d}}$ and $\gamma_{\mathrm{W}}^{\mathrm{n}}$ should be known.

On the basis of many studies [10–13] it is very probable that at the conditions of these experiments the quartz surface is covered with at least a monolayer water film. Therefore the components of $\gamma_{\mathrm{S}}^{\mathrm{d}}$ and $\gamma_{\mathrm{S}}^{\mathrm{n}}$ will be treated here as those resulting from the presence of the water film. Adsorption of water and hydrocarbons molecules is possible on such film. Moreover, it is even possible that around the water drop $\gamma_{\mathrm{sf}_1} \rightarrow \gamma_{\mathrm{W}}$ [10, 11].

From the literature [10, 11] one can find that the dispersion component of quartz surface free energy $\gamma_{\mathrm{S}}^{\mathrm{d}}$ equals $29.7\,\mathrm{mJ\,m^{-2}}$ and the non-dispersion component equals $91.3\,\mathrm{mJ\,m^{-2}}$ [13]. The values deal with a monolayer water film present on quartz surface. Then, knowing these values we can predict their

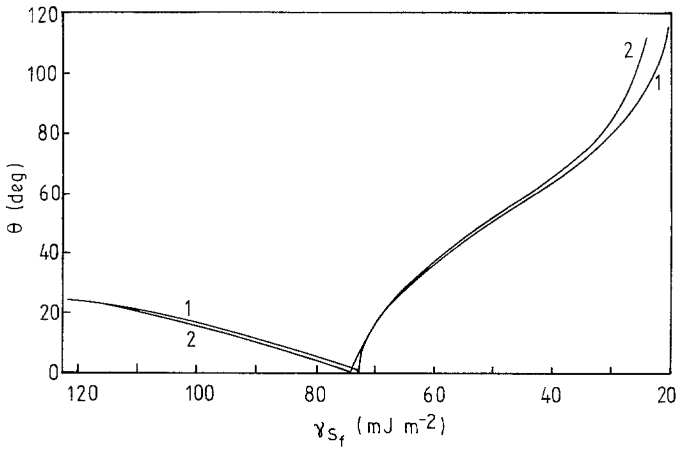

Figure 3 The dependence of the contact angle (θ) for a water drop on the surface free energy of quartz–monolayer water film–hydrocarbon film as calculated from Equation 4. Curve 1: values of θ calculated for n-heptane film. Curve 2: values of θ calculated for n-decane film.

possible changes resulting from the presence of hydrocarbon films.

Regardless of whether the hydrocarbon molecules absorb on the water film or disrupt it and adsorb on the bare surface of quartz the γ_S^d value can only decrease to γ_H (for a thick hydrocarbon film), i.e. surface tension of hydrocarbon, which practically results from the dispersion interactions only. Simultaneously, the non-dispersion component of the quartz surface free energy can reduce to zero.

With these boundary values of γ_S^d and γ_S^n, changes of the contact angle θ were calculated from Equation 4 as a function of the surface free energy of the quartz covered with a hydrocarbon film, γ_S. Thus, in consequence θ changes can be considered as a function of the hydrocarbon film thickness. These results are presented in Fig. 3. Curve 1 refers to n-heptane and curve 2 to n-decane film. These curves were constructed from the basis of the following assumptions.

(1) If $\gamma_S > \gamma_W$ then $\pi = \gamma_{Sf} - \gamma_W$.

(2) At the beginning of the alkane film formation $\pi_2 = 0$ and π_1 changes from 0 to $(\gamma_S^d - \gamma_H)$.

(3) At the second stage of the film formation $\pi_1 = \gamma_S^d - \gamma_H$, and π_2 changes from 0 to γ_S^n.

From Fig. 3 it is seen that these results are similar for heptane and decane.

The contact angle θ, values decrease to zero as the thickness of the alkanes film increases to what appears at γ_S value equal to $\gamma_W = 72.8\,\text{mJ}\,\text{m}^{-2}$. However, then θ values increase up to 115° (for n-heptane) and 111.9° (for n-decane) if $\gamma_S \rightarrow \gamma_H$, that is the surface tension of the alkane (20.3 and 23.9 mN m^{-1}, respectively). The calculations showed (Equation 4, Fig. 3) that for $\pi = \gamma_{Sf} - \gamma_W$ and $\pi_2 = 0$ changes of $0 < \pi_1 < (\gamma_S - \gamma_H^d)$ result in small changes of contact angles. Calculated values of θ for the above parameters are from 23.1 to 24.3° for heptane, and from 23.2 to 24.3° for decane. These values are close to the experimental ones 22 to 23° and 19°, respectively.

In the case of $\gamma_S \rightarrow \gamma_W$, and $\pi_1 = \gamma_S^d - \gamma_H$, and $\pi_2 = 0$ the contact angle values tend to zero. For $\gamma_S < \gamma_W$, and $\pi_1 = \gamma_S^d - \gamma_H$, increase of π_2 makes rapid increase of θ as calculated from Equation 4. Moreover, from the same Equation it results that for $\gamma_S < \gamma_W$, and $0 < \pi_1 < \gamma_H$, and $0 < \pi < W_S$ (work of water spreading on quartz surface covered with a monolayer water film and the alkane film for a given value of π_1) each value of θ laying in the range from 0 to 112 to 115° can possibly be obtained in the real experimental system.

The experiments and the calculations suggest that changes of θ as a function of the n-alkane film thickness is characterized by a curve possessing maxima and minima. This also explains similar changes of the flotation activity of quartz as a function of n-alkane film thickness [2] present on its surface. Determination of n-heptane film pressure on the quartz surface from zeta potential measurements [14] gave results dependent on the quartz pretreatment, and they were in the range from 4.28 to 9.38 mJ m^{-2}. These values are smaller than maximum value of $\pi_1 = \gamma_S^d - \gamma_H$ for $\pi_2 = 0$ (9.4 mJ m^{-2}).

Therefore, it seems that the alkane film, first of all, causes a decrease in the dispersion component of the surface free energy of the quartz surface on which there has already been present a water film, and maybe, causes decrease only to some extent the non-dispersion component of the energy γ_S^n.

This conclusion is in agreement with flotation results obtained on quartz wetted with the hydrocarbon, where only about 10% maximum recovery has been obtained (slightly higher than natural) despite the fact that 2 to 3 calculated monolayers of the film were present. This means, that the structure of the film is not uniform [14] and the polar forces still operate on the surface.

It is also possible to verify the conclusion through the calculation of the work of adhesion (W_A) of water to the quartz surface covered with water and the alkane film.

$$W_A = 2[(\gamma_S^d - \pi_1)\gamma_W^d]^{1/2} + 2[(\gamma_S^n - \pi_2)\gamma_W^n]^{1/2} \quad (5)$$

for $\pi_1 = 0$, $\pi_2 = 0$ (bare surface of quartz) $W_A = 187.4\,\text{mJ}\,\text{m}^{-2}$, and for $\pi_2 = 0$, $\pi_1 = \gamma_S^d - \gamma_W$, W_A equals 178.5 and 182.1 mJ m^{-2} for heptane and decane, respectively. It is clearly seen that only a small decrease in W_A is caused by the films, but the values are still well above the work of water cohesion (145.6 mJ m^{-2}). Hence, only a tiny effect is observed in the flotation activity of quartz wetted with n-alkane in comparison with the bare surface.

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