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STUDIES WITH A DERIVATOGRAPH OF THE PROPERTIES OF A WATER FILM ON A MARBLE SURFACE MODIFIED BY TETRADECYLAMMONIUM CHLORIDE (TDACl)

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The properties of water layers on bare marble and on marble samples covered with various amounts of tetradecylammonium chloride (TDACl) after flotation were investigated by thermal analysis methods. The dependences of the layer thickness, activation energy, enthalpy and entropy of the bonded water *vs.* the amount of TDACl previously deposited on the marble surface were determined. The results obtained and the literature data were used to propose an interpretation of the changes caused in these parameters by the coverage of the marble surface with TDACl molecules. A correlation between these parameters and the changes in water structure and marble flotatibility is also presented.

Useful minerals exist in nature together with useless rock minerals. In mechanical mineral enrichment processing in aqueous media, mainly a flotation method is used. More than 60% of the minerals are concentrated by this method. Flotation is a very complicated process because it takes place in heterogeneous, multiphase and dynamic systems [1]. This separation process involves a large number of individual microprocesses taking place simultaneously and successively. The water layers on mineral surfaces play a very important role in flotation, because the thickness and stability of the vicinal water layers are of major significance during the adhesion of air bubbles to mineral grains [2–5]. The properties of water layers adsorbed on mineral surfaces are very different from those of bulk water [6, 7]. as a result of the polar and dispersion interactions between the water molecules and the mineral surfaces. They form an energetic barrier during the adhesion of air bubbles to mineral grain surfaces. In flotation, unstable films are a necessary condition for particle attachment to bubbles. In general, thin films are made unstable by hydrophobizing previously hydrophilic particles by means of collectors. In spite of

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the use of collectors, particles of useful minerals are found in postflotation slimes, e.g. about 3% in the flotation of sulphur, and 2030% in the flotation of coal slimes.

At present, knowledge on the properties of water films and their role in flotation processes is still far from complete. Sor far, only a few papers have dealt with the problem of the qualitative dependence between the adsorption of collectors on mineral surfaces and the properties of water films [1–5]. Accordingly, the present studies were undertaken to investigate the role and quantitative properties (thickness, thermodynamic functions, structure) of water films on marble surfaces containing preadsorbed TDACl.

Experimental

Marble exists in nature as a useless rock accompanying useful minerals, e.g. sulphur, coal and quartz. Natural marble from mineralogical specimens (grain size 0.12–0.3 mm) was used for the measurements. The surface area determined by the nitrogen thermodesorption chromatographic method [8] was 0.06 m^2/g. Marble samples dried at 110° were coated with tetradecylammonium chloride (TDACl). TDACl is a typical collector in the flotation of quartz and barite. It was obtained in our laboratory from pure tetradecylamine and was purified by crystallization. This reagent was selected from several collectors used in mineral flotation because of its high boiling point (above 250°). This high boiling point was a very important factor, because after flotation the samples were subjected to thermodesorption of water at 150°. The mineral was coated with collector by a method similar to that used during the deposition of the stationary phase in gas chromatography [9]. The 3 g sample was immersed in 4 ml of TDACl solution in methanol containing a suitable amount of collector [10]. The solvent was evaporated at 50°, and the samples were then dried at 50° for 4 h. The amount of collector deposited on the mineral surface was expressed as the number of statistical monolayers, assuming that the surface area occupied by one TDACl molecule is 20 Å^2. This value corresponds to the cross-section of a hydrocarbon chain. Since the investigated system chosen in this way was only a model, flotation tests on marble from aqueous TDACl solutions of various concentrations were also carried out for purposes of comparison. The samples previously covered with TDACl were subjected to flotation in double-distilled water in the pneumatic apparatus for 3 min. The nitrogen flow rate was 60 ml/min. The amounts floated out and rejected were filtered (after drying) on paper filter.

A Q-1500 D derivatograph (MOM, Hungary) was used in our investigations [11]. This apparatus permits the following complex measurements:

1. Dynamic measurements of water thermodesorption from the marble surface

The 1.5 g marble samples were placed in a platinum crucible and thermodesorption measurements were carried out in the temperature range 20–150°. The furnace heating rate was 0.6, 1.25 or 2.5 deg/min. The following curves were recorded: sample mass loss TG curve, differential sample mass loss DTG curve, temperature difference DTA curve between the sample investigated and the standard sample, and the temperature increase T curve.

2. Quasi-isothermal measurements

The 1.4 g marble samples were transferred into a platinum crucible and thermodesorption measurements were carried out under quasi-isothermal conditions in the temperature range 20–150°. The furnace heating rate was 6 deg/min. The relationship TG = $F(T)$ was recorded.

3. Measurements by the combined thermal analysis and chromatographic step profile method

The 150 mg samples were placed on a suitable holder of a modified derivatograph balance [13]. The samples were heated up to 130° in a continuous nitrogen flow in order to remove water from the marble surface. The samples were then cooled to the measurement temperature (20°). Nitrogen saturated with water vapour was passed through the measurement cell at 20°. Under these conditions, the adsorption of water on the marble surface takes place until adsorption equilibrium is established (plateau region in the TG curve). After complete saturation of the sample with water vapour from the gas phase, water is desorbed by a flow of dry nitrogen at 20°. From the TG curve the adsorption capacity of the sample (maximum water adsorption from the gas phase at 20°) was determined.

Results and discussion

1. Investigations of properties of water films on a bare marble surface

Figure 1 presents the results of measurements of water thermodesorption from a bare marble surface at a furnace heating rate of 0.6 deg/min. It results from the date presented in this Figure that there are 3 peaks in the DTG and DTA curves, which correspond to water desorption values of 0.56 mmol/g (peak III), 1.23 mmol/g (peak II) and 14.7 mmol/g (peak I). The existence of low-temperature peaks in the

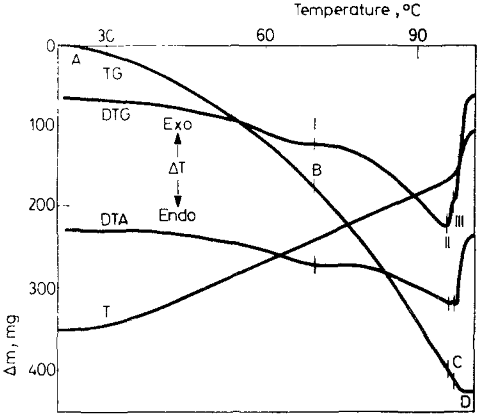

Fig. 1 The T, DTA, TG and DTG curves of the thermodesorption of water from the bare marble surface

DTA curve may be ascribed to differences in the bonding energy of the water molecules with the barite surface [12]. In order to make the interpretation of the results presented in Fig. 1 more precise, quasi-isothermal measurements and also measurements of water adsorption from the gas phase were carried out.

Figure 2 presents the curve produced from the data obtained during quasi-isothermal evaporation of water from a bare marble surface. In this curve there are three inflection points, corresponding to temperatures of 96° (point A), 103° (point B, $a_B = 15.8$ mmol/g) and 105° (point C, $a_A = 0.49$ mmol/g). Figure 3 presents the TG curve of the adsorption and the desorption of water on and from the bare marble surface at 20°, obtained using the combined method. This curve shows that 0.5 mmol/g of water can be adsorbed from the gas phase onto the

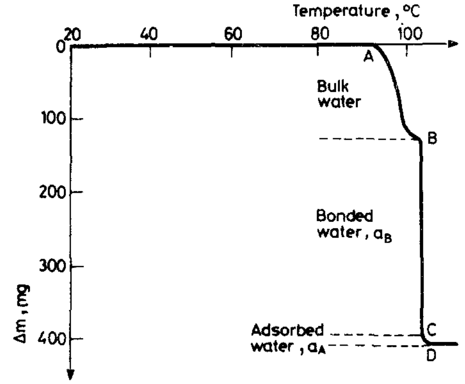

Fig. 2 The squasi-isothermal curve of the desorption of water from the bare marble surface

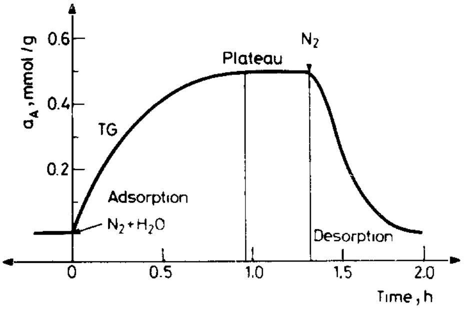

Fig. 3 The TG curve corresponding to the adsorption and desorption of water vapour on and from the bare marble at 20°, obtained using the combined method

marble surface. It seems very interesting that apart from different measurement temperatures and methods, some steps of the water thermodesorption process may be correlated with the amount of water adsorbed from the gas phase. The maximum adsorption value (Fig. 3) corresponds to the inflection point in Fig. 2 and peak III (point C) in Fig. 1. Thus, region CD in Figs 1 and 2 corresponds to the thermodesorption of the water most strongly bonded to the marble surface. The evaporation of this water requires the greatest amount of energy. Region AB in Figs 1 and 2 corresponds to the desorption of bulk water. Region BC corresponds to the desorption of those water layers which have a modified structure (bonded water in pore spaces and capillaries). This water structure is more liquid-like. The thickness of the water layers with a modified structure is not known exactly. There are some data in the literature concerning the thickness of water layers on mineral surfaces [6, 7, 14, 15]. They are formed as a result of interaction between the surface and the water molecules closest to it with induction of certain structures in the subsequent layers. The critical water film thickness at which disruption of the film may appear is 15–60 nm, but under dynamic conditions of mineral processing this value may be higher [16].

Before all free active centres on the marble surface have been occupied by water molecules (region CD, Figs 1 and 2), aggregates of water bonded by hydrogen-bonds may be formed. Such a mechanisms results from the interrelation between the adsorption energy, the bonding energy in the aggregates and the entropy. Since the hydrogen-bond energy is 25.05 kJ/mol and the condensation heat is 43.89 kJ/mol, it can be predicted that the energetically preferred process is agglomerate formation, rather than the formation of single hydrogen-bonds [17]. These aggregates are formed on the polar and dispersion-active sites on the marble surface. The investigations carried out in our laboratory confirmed the heterogeneity of this surface. The measurements of heptane and methanol adsorption on the marble surface were performed in a manner similar to that in water adsorption determination (Fig. 3), by applying the combined method (point 3 in the Experimental). The adsorption isotherms of heptane, methanol and water were drawn from the TG curves by using the method described previously [18]. From these adsorption isotherms, the film pressure π values were determined as a function of the adsorbed amount. The π values were calculated from the Bangham and Rozouk equation [19]. From the dependence between the π and adsorption values and based on a method described in [20], the dispersion γ_s^d and polar γ_s^p components of the free surface energy of the marble were calculated. The calculated values are $\gamma_s^d = 67$ mJ/m^2 and $\gamma_s^p = 101$ mJ/m^2, and are similar to those presented in [20]. The changes in the water film properties on the surface appear to be connected with both dispersion and polar interaction between the water molecules and the marble surface (dispersion components: 21.8 mJ/m^2 and 67 mJ/m^2; polar components: 51 mJ/m^2 and 101 mJ/m^2, respectively).

The suggestion relating to the structure of the water layer may be confirmed by calculation of the activation energy of the water molecules, i.e. the energy of the bonds formed between the water molecules. The activation energy ΔE was calculated from the Piloyan equation [21]:

$$\ln \Delta T = C - \frac{E}{RT} \tag{1}$$

where ΔT is the deviation of the DTA curve from the baseline and C is a constant.

The ΔE value for the water molecules on the marble surface corresponding to region BD is 42.8 kJ/mol. This is higher than the value needed for the destruction of hydrogen-bonds in bulk water ($\Delta E_L = 25.08$ kJ/mol). On the basis of quantum mechanics laws, Klier and Zettlemoyer [17] have calculated the energy of bonds formed between molecules of vicinal water in the range from dimer to open pentamer; the energy values vary from 12.75 kJ/mol to 48.7 kJ/mol. From a comparison of the experimentally determined ΔE value and those calculated by Klier and Zettlemoyer, it results that in region BD water structures of cyclic tetramer type may exist. These aggregates are the most compact and ordered and the most strongly bonded to the marble surface (see below: Fig. 8, minimum entropy value -92 J/mol deg). The adsorbed molecules are oriented because of dipole-dipole interactions (adsorbed water). Far from the surface there is a bulk water layer where some structural forms exist (clusters or polymorphic high-pressure ice structures). These are presumed to be in equilibrium with single molecules. Between the adsorbed water and the bulk water, there is a partially disordered layer of bonded water. Its structure results from interactions of the water molecules with the adsorbed layer and the bulk water [22].

The experimental results presented in Figs 1 and 2 suggest that the desorption of water bonded to the marble surface occurs in two steps: moreover, they confirm a hypothetical model of bonded water [6].

2. *Effect of TDACl on properties of water bonded to the marble surface*

With the three above-mentioned methods of bare marble examinations, analogous measurements were carried out on marble samples after flotation (recovery and reject) previously coated with various amounts of TDACl (0.25, 0.5, 0.75 and 1 monolayer).

Figure 4 presents the dependence of the adsorption capacity a_A (maximum adsorption value) on the amount of TDACl deposited on the marble surface, determined during the dynamic adsorption of water from the gas phase. This Figure indicates that the a_A value descreases monotonously for the samples floated out (curve 1), but does not change for the reject samples (curve 2). The a_A values for the reject samples are near the value for the bare marble sample. In the same way, there are changes in the amount of water a_B on the marble surface *vs.* the coverage N of the surface with TDACl, determined with the quasi-isothermal method (Fig. 5).

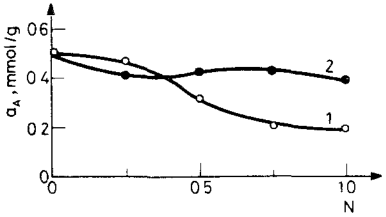

Fig. 4 Amounts of adsorbed water a_A as a function of the TDACl statistical monolayer coverage of the marble surface obtained using the combined method (curve 1 – recovery samples, curve 2 – reject samples)

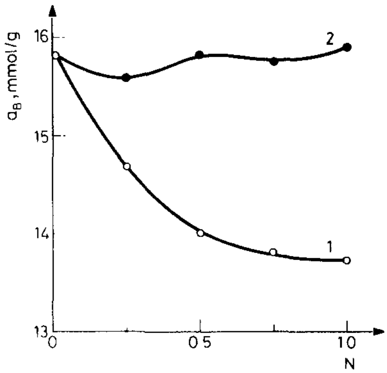

Fig. 5 Amount of bonded water a_B as a function of the TDACl statistical monolayer coverage of the marble surface obtained using the quasi-isothermal method (curve 1 – recovery samples, curve 2 – reject samples)

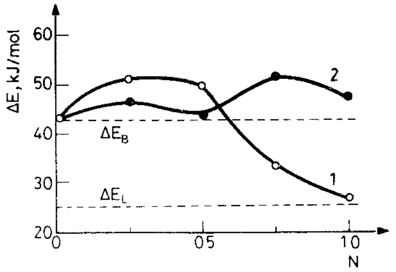

Fig. 6 The relationship between the activation energy of the water molecules and the statistical monolayer coverage of TDACl deposited on the marble surface (ΔE_B – activation energy of the bonded water on the bare marble surface, ΔE_L – activation energy of bulk liquid water)

Figures 4 and 5 indicate that when the coverage value attains 1 monolayer of TDACl, the a_A and a_B values become constant.

Figure 6 presents the changes caused in the activation energy ΔE values of the water molecules by the presence of TDACl on the marble surface (curve 1—recovery samples, curve 2—reject samples). The ΔE values were calculated from Eq. (1) on the basis of the T and DTA curves from the dynamic measurements of water thermodesorption. Curve 1 in this Figure shows the that water molecules have the greatest activation energy when the marble surface is covered by 0.25 and 0.5 TDACl monolayer. The smallest ΔE value exists when the marble surface is covered by $N = 1$ TDACl monolayer. This value is comparable with the activation energy value ΔE_L for bulk water molecules. Curve 2 depicts the above relationship for the reject samples. From this curve, it appears that the ΔE values are somewhat larger than those of water adsorbed on the bare marble surface.

Figures 7 and 8 present the changes caused in the enthalpy and entropy of the bonded water molecules by changes in the amount of TDACl deposited on the marble surface. The enthalpy ΔH and entropy ΔS changes were determined on the basis of dynamic measurements of water thermodesorption from the marble samples (carried out at three derivatograph furnace heating rates) and on the basis of the Kissinger equations [23]:

$$\Delta H = R\frac{\mathrm{d}\cdot\ln[T_m^2(\mathrm{d}T_p/\mathrm{d}t)]}{\mathrm{d}(1/T_m)} \tag{2}$$

$$\Delta S = R\left[\frac{\Delta H}{RT_m} + \ln\frac{\Delta H}{R} - \ln\frac{T_m^2}{\mathrm{d}T_p/\mathrm{d}t} - \ln\frac{k\cdot T_m}{h}\right] \tag{3}$$

where T_m is the temperature of the extreme effect point in the DTA curve, T_p is the sample temperature, k is the Boltzmann constant, h is the Planck constant and R is the gas constant.

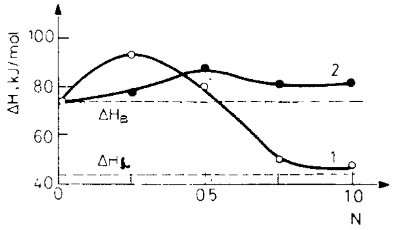

Fig. 7 The enthalpies of water evaporation from the surface as a function of the TDACl statistical monolayer coverage deposited on the marble samples (ΔH_B – enthalpy of evaporation of the bonded water from the bare marble surface, ΔH_L – enthalpy of evaporation of bulk liquid water)

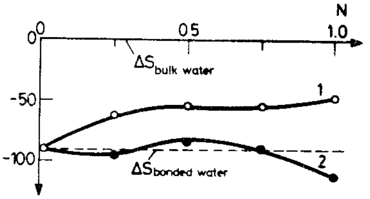

Fig. 8 The relationship between the entropies of the water molecules and the statistical monolayer coverage of TDACl on the marble surface ($\Delta S_{\text{bonded water}}$ – entropy of the water molecules on the bare marble surface)

It appears from Fig. 7 (curve 1—recovery samples) that the relationship $\Delta H = f(N_{\text{TDACl}})$ reaches a maximum in the presence of 0.25 TDACl monolayer, while a minimum is reached when the marble surface is covered with 0.75 or 1 monolayer of TDACl. The enthalpy value corresponding to the minimum is 48.3 kJ/mol, and is approximately equal to the condensation heat of liquid water, $\Delta H_L = 43.89$ kJ/mol. Figure 8 (curve 1—recovery samples) presents the changes caused in the entropy ΔS of the bonded water molecules by changes in the amount of TDACl deposited on the marble surface. The relationship presented in this Figure is characterized by increasing ΔS values. This relationship is similar to those obtained on barite covered with TDACl [24], on bare quartz [25] and on other mineral surfaces [26] as a function of the amount of water adsorbed. Curves 2 in Figs 7 and 8 show analogous dependences for the reject samples. The ΔH and ΔS values for marble samples covered with TDACl are similar to those for bare marble samples.

Figure 9 A presents the dependence of the percentage recovery W on the number of statistical TDACl monolayers N, and Fig. 9 B the dependence of the percentage recovery W on the initial collector concentration C [10]. The upper scales in both Figures denote the collector consumption, i.e. the amount of reagent introduced to the flotation system per dry minerals mass unit (expressed in g/t). It can be seen that

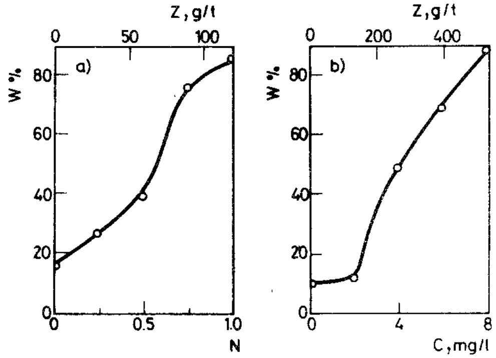

Fig. 9 The flotability of marble (% recovery) as a function of the TDACl amount deposited on the barite surface (A) and the initial concentration of the TDACl solution (B) lower scales. The upper scales denote the collector consumption

the flotability increases with increase of the surface coverage with a collector (Fig. 9 A) and with increase of the collector concentration (Fig. 9 B). The flotability reaches a maximum value (above 86%) for 1 TDACl monolayer and for 8 mg/l of TDACl. These are the typical flotation curves. The shapes of the two curves are quite alike, which demonstrates the relatively strong adsorption of the collector from aqueous solution (its strong bonding with the marble surface). Differences in reagent consumption values became clear because some portion of the reagent remains in the solution. Nevertheless, the similar shapes of the two curves permit the assumption that the model system selected in this way reflects the real flotation systems fairly exactly.

An interpretation of the changes in the parameters presented in Figs 4–8 in connection with the flotation parameters requires a consideration of all changes in structure, layer thickness and interaction of both TDACl and bonded water. According to the present opinion, if the surface coverage is less than 1 monolayer, TDACl is adsorbed on the marble surface via its polar part $[C_{14}H_{29}NH_3]^+Cl^-$ (chemical interactions with polar active sites), while the hydrocarbon chain is directed outwards. The dissolution of the TDACl molecules deposited on the surface in this way seems impossible. Derivatographic investigations of non-floated marble samples covered with 1 monolayer of TDACl showed no differences in the investigated parameters in comparison with the floated sample. The results of flotation tests (Fig. 9) also suggest that dissolution does not take place (the increase in surface coverage is accompanied by an increase in flotability). At higher coverages, microcrystals or molecular clusters possessing properties similar to those of solid TDACl can be formed [10]. For coverages thicker than 1 monolayer, a certain solubility of the microcrystals or molecular clusters may appear. The constant flotability (Fig. 9) suggests such a possibility. Nevertheless, the aim of this paper was to examine the influence of TDACl on the water properties close to the marble surface covered with the collector in the range from 0 to 1 monolayer.

The adsorption of 0.25 TDACl monolayer occurs on the most polar active centers of the marble surface. This causes a reduction of the mineral surface-water interactions and consequently a decrease in the amount of bonded water (Figs 4 and 5, curves 1), accompanied by ΔE, ΔH and ΔS changes (Figs 6–8, curves 1). The presence of 0.5 TDACl monolayer on the marble surface results in an increase in the number of hydrophobic TDACl molecules on the marble surface, and in the formation or induction of cyclic tetramer-type water clusters (from a comparison of the ΔE data in Fig. 6 and those presented in [17]). The water molecules contained in clusters have the greatest intermolecular bonding and reduced mobility; they have more restricted translational and rotational motion, their structure is better ordered [17], and thus they have lower entropy values than that of the bulk liquid phase (Fig. 8, curve 1). The destruction of such a structure requires a greater amount of energy in comparison with that on the bare marble surface (Fig. 7, curve 1). The presence of hydrophobic molecules of TDACl in the vicinity of the clusters of water may increase the coordination number of the water molecules up to 5. Such water has a lower energetic level than water possessing a coordination number of 4 in liquid water [27]. As a result, the number of water molecules in the clusters situated close to the hydrophobic surface increases; this may be caused by the entry of water monomers into the free spaces in the cluster lattices [22, 28]. The amount of these water molecules may be higher, but the thickness of this water layer may be lower in comparison with that deposited on the bare marble surface, because of the greater condensation of the molecules. This is the reason why air bubbles have easier access to the marble surface during flotation (improvement of flotation parameters, Fig. 9).

Increase of the TDACl amount on the marble to 1 monolayer causes a complete coverage of its polar surface with the collector, and further changes in the bonded water structure. The investigations carried out in our laboratory [29] showed that coverage of the marble surface with 1 monolayer of TDACl leads to a decrease in the polar free surface energy to 0, and in the dispersion energy from 67 mJ/m^2 to the value corresponding to the free energy of the hydrocarbon surface (25–30 mJ/m^2). It may be concluded that TDACl molecules adsorbed on polar sites of the marble surface also reduce the dispersion interactions between the surface and the water. In the marble/water system, such a coverage with TDACl provides a complete reduction of the polar interactions and a considerable decrease in the dispersion interactions between the marble surface and the water. The changes in the properties of the water films, are very small and these properties are very similar to those in the bulk liquid phase (Figs 6–8, curves 1). The TDACl layer reduces the marble-water interactions and the induction of long-range water structures seems impossible. Hydrophobization of the marble surface allows the formation of a water structure with characteristics similar to those of the bulk water. The ΔE value of such water molecules is 26.5 kJ/mol (Fig. 6, curve 1) and indicates the formation of a linear or cyclic trimer-type structure. The mobility of the water molecules is greater than the mobility of the molecules bonded to the bare marble surface. The entropy of these molecules is between the entropies of the bonded and the bulk water (Fig. 8, curve 1). The enthalpy then has a minimum value, comparable to the condensation heat of liquid water (Fig. 7, curve 1). These water films may be referred to as "hydrophobic hydration" [6], which appears as a result of the dispersion interactions between the water and the marble surface. The water film on the marble surface is unstable and has a loose structure in comparison with that for the bare surface. The presence of 1 TDACl monolayer on the marble surface reduces both the thickness (calculated critical film thickness $h_{\mathrm{crit}} = 23.1$ nm) and the energetic barrier of the bonded water layer. This facilitates the flotation process [1–4]. When the flotation process is carried out under dynamic conditions, such a water film may be destroyed spontaneously. Under these conditions, air bubbles can remove the water layers and reach as far as the dry marble surface covered with TDACl.

As mentioned above, the changes in the properties of the water layers on the surface of reject samples (Figs 4–8, curves 2) are almost the same as those of the bare surface. The marble surface is a heterogeneous one. The separate grains do not seem equivalent in their surface properties (energy). Thus, the deposited collector layer is not uniform in thickness, and "patches" of molecules are probably formed on the sites of highest energy. The same holds for the separate grains of the mineral. Those of higher average surface (at least at coverages of a few monolayers). The grains with a lower average surface energy remain "clean", or are covered insignificantly with collector. Therefore, almost no influence of the collector layer on the surface water layers was observed for the reject. This seems the main reason why marble does not float totally, even at a coverage of one statistical monolayer. Although the experiments described above were carried out on simplified model systems, a similar distribution of the collector molecules should occur in real flotation systems where collector layers are formed on adsorption from water.

Conclusions

Water layers possessing different properties than those of bulk water are formed spontaneously on a bare marble surface, as a result of polar and dispersion interactions between the water molecules and the solid surface. The efficiency of the flotation process is dependent on the properties of these layers. Flotation collectors change these properties, as demonstrated by the calculation of some thermodynamic quantities. They lead to the formation of layers possessing properties similar to those of bulk water and to the increase in flotability of a mineral. Nevertheless, some grains of mineral do not float, because the properties of the surface water layers on these grains are similar to those on the bare surface. This seems to be due to the non-equivalent surface properties of the separate grains, and mainly the surface energy distribution. This leads to the non-uniform distribution of the collector on these grains and to the partial flotability of the mineral. The conditions of collector adsorption should provide the most uniform collector distribution for achievement of the total flotability of a mineral.

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Zusammenfassung — Eigenschaften von Wasserfilmen auf unbeschichteten und mit Tetradecylammoniumchlorid (TDACl) in unterschiedlichen Mengen bedeckten Marmorproben wurden nach Flotation thermoanalytisch untersucht. Die Abhängigkeit der Schichtdicke, der Aktivierungsenergie und der Enthalpie und Entropie des gebundenen Wassers von der Menge des vorhergehend auf die Marmoroberfläche aufgebrachten TDACl wurden ermittelt. Die durch die Bedeckung der Marmoroberfläche mit TDACl verursachten Veränderungen dieser Parameter werden anhand der erhaltenen Resultate und von Literaturangaben interpretiert. Beziehungen zwischen diesen Parameters und Veränderungen der Wasserstrukturen und der Flotierbarkeit des Marmors werden angegeben.

Резюме — Термическими методами анализа изучены свойства слоев воды на поверхности чистого мрамора и образцах мрамора, покрытых различным количеством тетрадециламмоний хлорида (ТДАХ). Определена зависимость толщины слоя воды, энергии активации, энтальпии и энтропии связанной воды от степени покрытия ТДАХ. На основании полученных результатов, а также исходя из литературных данных, была предложена интерпретация изменения этих параметров, вызванных покрытием поверхности мрамора ТДАХ. Представлена также корреляция между этими параметрами, изменением откуртуры воды и флотационной способностью мрамора.