

## **INVESTIGATIONS OF WATER FILM PROPERTIES ON BARITE SURFACE CONTAINING PREADSORBED TETRADECYLAMMONIUM HYDROCHLORIDE (TDACl)**

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### **ABSTRACT**

Investigations of the properties of water layers on bare barite and on barite samples covered with various amounts of TDACl after flotation are described. A thermal analysis method was used in our investigations. The relations between layer thickness, activation energy, enthalpy and entropy of bonded water and the amount of TDACl previously deposited on the barite surface were determined. On the basis of the results obtained and on the literature data an interpretation of these parameter changes caused by the barite surface coverage with TDACl molecules is proposed. Correlation between these parameters and the changes of water structure and barite flotability is also presented.

### **INTRODUCTION**

In mineral processing the separation of various mineral grains is very often obtained by flotation. In these methods a selective separation results from some differences in the surface properties (wettability) of the minerals. These differences are further enlarged by application of suitable flotation reagents (collectors) [1].

According to present opinions the changes in surface water film properties (film thickness, structure, surface energy of water placed between a bubble and a solid surface) play a dominant role in minerals enrichment processes [1–4]. The properties of water molecules adsorbed on the surface of minerals are much different from those of bulk water [5–7] and they form an energetic barrier during the adhesion of an air bubble to the mineral grain surface. Regulation of properties of these water layers makes it possible to control the enrichment process.

In barite flotation TDACl may be used as a collector; therefore an investigation of the influence of TDACl on the water film properties at barite surfaces was carried out. This paper presents an examination of the effect of TDACl on water film thickness as well as its energetic properties

accompanying the water adsorption on the barite surface, using the thermal analysis method.

## EXPERIMENTAL

Natural barite from mineralogical specimens (grain size 0.06–0.1 mm) was used for the measurements. The surface area determined by the nitrogen thermodesorption chromatographic method [8] was  $0.136 \text{ m}^2 \text{ g}^{-1}$ . Barite samples dried at  $110^\circ\text{C}$  were coated with tetradecylammonium hydrochloride. The TDACl was obtained in our laboratory from pure tetradecylamine and purified by crystallization. This reagent was selected from several collectors used in mineral flotation because of its high boiling point (above  $250^\circ\text{C}$ ). This high boiling point was a very important factor because after flotation the samples were subjected to thermodesorption of water at  $150^\circ\text{C}$ . The mineral was coated with the collector by a method similar to that used during deposition of stationary phases 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]. Solvent was evaporated at  $50^\circ\text{C}$  and then the sample was dried at  $50^\circ\text{C}$  for 4 h. The amount of collector deposited on the mineral surface was expressed as a number of statistical monolayers, assuming that the surface area occupied by one TDACl molecule is  $20 \text{ \AA}^2$ . This value corresponds to a cross-section of a hydrocarbon chain. Since the investigated system chosen in this way was a model only, flotation tests of barite from aqueous TDACl solutions of various concentrations were also carried out for comparison. The samples previously covered with TDACl were subjected to flotation in double-distilled water in the pneumatic apparatus for 3 min. Nitrogen flow rate was  $60 \text{ ml min}^{-1}$ . The amount floated out was filtrated and weighed (after drying) on the paper filter.

Derivatograph Q-1500 D (MOM Hungary) was used in our investigations. This apparatus permits the following complex measurements:

### *Dynamic measurements of water thermodesorption from the barite surface*

The 2 g barite samples were placed in a platinum crucible and thermodesorption measurements [11] were carried out in the temperature range  $20\text{--}150^\circ\text{C}$ . Furnace heating rates were 0.6, 1.25 and  $2.5^\circ\text{C min}^{-1}$ . The following curves were plotted: sample mass loss TG curve, differential sample mass loss DTG curve, temperature difference between the sample investigated and standard sample DTA curve as well as temperature increase  $T$  curve.

### *Quasi-isothermal measurements*

The 1.5 g barite samples were transferred into a platinum crucible and thermodesorption measurements under quasi-isothermal conditions [11] were carried out in the temperature range  $20\text{--}150^\circ\text{C}$ , with a furnace heating rate of  $6^\circ\text{C min}^{-1}$ . The relationship  $\text{TG} = f(T)$  was plotted.

*Measurements realized by combined thermal analysis and chromatographic step profile method*

The 150 mg samples were placed on a suitable holder of a modified derivatograph balance [12]. Samples were heated to 130 °C under continuous nitrogen flow in order to remove water from the barite surface. Samples were then cooled to the measurement temperature (20 °C). Nitrogen saturated with water vapour was passed through the measurement cell at 20 °C. Under these conditions adsorption of water on the barite surface takes place until adsorption equilibrium is established (the plateau region of the TG curve). After the complete saturation of the sample by water vapour from the gas phase, water is desorbed by passing dry nitrogen at 20 °C. From the TG curve, the samples' adsorption capacity (maximal water adsorption from gas phase at 20 °C) were determined.

## RESULTS AND DISCUSSION

*Investigations of water film properties on the bare barite surface*

Figure 1 presents the results of water thermodesorption measurements from the bare barite surface with a furnace heating rate of 0.6 °C min<sup>-1</sup>. There are 3 peaks on the DTG and DTA curves which correspond to 0.12 mmol g<sup>-1</sup> (peak III), 2.25 mmol g<sup>-1</sup> (peak II) and 12 mmol g<sup>-1</sup> (peak I) of water desorption. The existence of low temperature peaks on the DTA curve may be ascribed to differences in bonding energy of water molecules with the barite surface [11].

In order to interpret the results presented in Fig. 1, more precise quasi-isothermal measurements and also measurements of water adsorption from the gaseous phase were carried out.

Figure 2 presents the curve determined by the data obtained during quasi-isothermal evaporation of water from the bare barite surface. On this curve there are three inflection points corresponding to temperatures of 101 °C (point A), 103 °C (point B,  $a_B = 11.3 \text{ mmol g}^{-1}$ ) and 105 °C (point C,  $a_A = 0.347 \text{ mmol g}^{-1}$ ). Figure 3 presents the TG curve of the adsorption of water on and desorption from bare barite surfaces at 20 °C obtained using the combined method. This curve indicates that 0.344 mmol g<sup>-1</sup> of water can be adsorbed from the gaseous phase on the bare barite 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 maximal adsorption value (Fig. 3) corresponds to the inflection C point in Fig. 2 and peak III (point C) in Fig. 1. Thus the region CD in Figs. 1 and 2 corresponds to thermodesorption of the water most strongly bonded to the barite surface. Evaporation of this water requires the greatest amount of

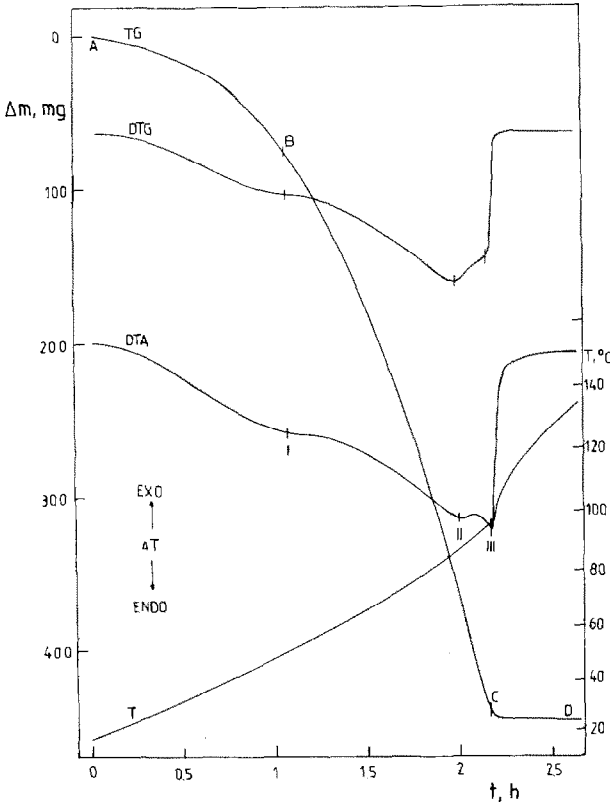


Fig. 1. Dynamic thermal curves of water thermodesorption from the bare barite surface.

energy. The region AB in Figs. 1 and 2 corresponds to the desorption of bulk water. Region BC corresponds to 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 of this modified structure is not known exactly. There are some data in the literature concerning the thickness of water layers on the mineral

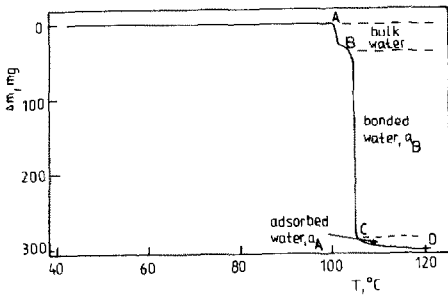


Fig. 2. Quasi-isothermal curve of water desorption from the bare barite surface.

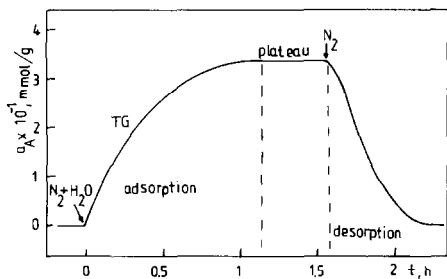


Fig. 3. The TG curve corresponding to adsorption and desorption of water vapour on and from bare barite at 20 °C, obtained using the combined method.

surfaces: 40 nm [13],  $10^4$  nm [14] and 150 nm [6,7]. These layers are formed as a result of interaction between the surface and the water molecules closest to it and the induction of certain structures in subsequent layers. Critical water film thickness when the disruption of the film may appear is 15–60 nm; however, in dynamic conditions of mineral processing this value may be higher [15].

Before all the free active centres on the barite 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 mechanism results from the interrelation between adsorption energy, bonding energy in aggregates and entropy. Because hydrogen bond energy is  $25.05 \text{ kJ mol}^{-1}$  and condensation heat is  $43.89 \text{ kJ mol}^{-1}$ , it can be predicted that the energetically-preferred process is agglomerate formation rather than formation of single hydrogen bonds [16]. These aggregates are formed on the polar and dispersion active sites on the barite surface. The investigations carried out in our laboratory confirmed the heterogeneity of this surface. The measurements of heptane and methanol adsorption on barite surfaces in a way similar to that in water adsorption determination (Fig. 3) by applying the combined method (see Experimental above) were performed. Adsorption isotherms of heptane, methanol and water were drawn from the TG curve using the method described previously [17,18]. From these adsorption isotherms the film pressure  $\pi$  values were determined as a function of the adsorbed amount. Film pressure  $\pi$  values were calculated from the Bangham and Razouk equation [19]. From the relation between  $\pi$  and adsorption values, and based on the method described in ref. 20 the dispersion  $\gamma_s^d$  and polar  $\gamma_s^p$  components of the free surface energy of barite were calculated. The calculated values are  $\gamma_s^d = 66.7 \text{ mJ m}^{-2}$  and  $\gamma_s^p = 78 \text{ mJ m}^{-2}$ . The change in water film properties on the surface seems connected with both dispersion and polar interaction between water molecules and the barite surface (dispersion components 21.8 and  $66.7 \text{ mJ m}^{-2}$ ; polar components 51 and  $78 \text{ mJ m}^{-2}$ ).

Suggestions relating to the structure of the water layer in the region BD may be confirmed by calculation of the activation energy of water mole-

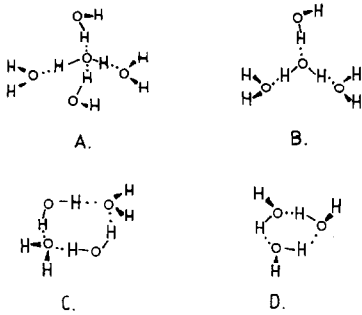


Fig. 4. Geometry of some water clusters (taken from Klier and Zettlemoyer [16]): A, pentamer ( $-33.1 \text{ kJ mol}^{-1}$ ); B, central tetramer ( $-30.35 \text{ kJ mol}^{-1}$ ); C, cyclic tetramer ( $-43.89$  to  $-17.97 \text{ kJ mol}^{-1}$ ); D, cyclic trimer ( $-23.4$  to  $-8.8 \text{ kJ mol}^{-1}$ ).

cules, i.e. energy of interactions between water molecules. Activation energy  $\Delta E$  was calculated from the Piloyan equation [21]

$$\ln \Delta T = C - (\Delta E/RT) \quad (1)$$

where  $\Delta T$  is the deviation of the DTA curve from the base line and  $C$  is a constant.

The  $\Delta E$  value of water molecules on the barite surface corresponding to the region BD is  $36.8 \text{ kJ mol}^{-1}$ . This is higher than that needed for destruction of hydrogen bonds in bulk water ( $\Delta E_L = 25.08 \text{ kJ mol}^{-1}$ ). On the basis of quantum mechanic laws Klier and Zettlemoyer [16] have calculated the energy of bonds formed between molecules of vicinal water in the region, from dimer to open pentamer: the energy values change from  $12.75$  to  $48.7 \text{ kJ mol}^{-1}$ . From a comparison of experimentally determined  $\Delta E$  values and those calculated by Klier and Zettlemoyer it follows that in

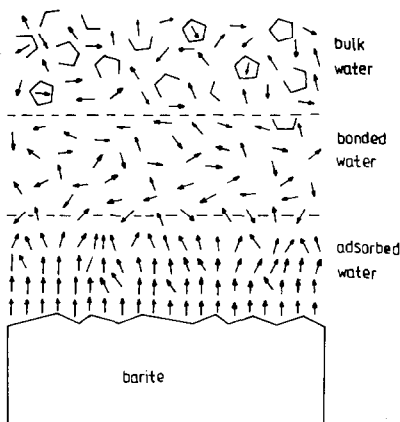


Fig. 5. The modified schematic structure of the water layer on the bare barite surface (taken from Drost-Hansen [22]).

the region BD water structures of the pentamer type may exist (Fig. 4A). These linear aggregates are the most compact and ordered ones and the most strongly bonded to the barite surface (see below: the minimal entropy value is  $-117.1 \text{ J mol}^{-1} \text{ K}^{-1}$ ).

Figure 5 presents a schematic structure of bonded water layers on the polar barite surface (taken from the paper of Drost-Hansen [22]). The adsorbed molecules are oriented because of dipole-dipole interaction (adsorbed water). Far from the surface there is a bulk water layer where some structural forms exist (clusters or polymorphic high pressure ice structures). They are supposed 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 water molecules with the adsorbed layer and bulk water [22].

Experimental results presented in Figs. 1 and 2 suggest that the desorption of water bonded with the barite surface occurs in two steps and, moreover, they confirm a hypothetical model of bonded water [6,7].

#### *Effect of TDACl on properties of water bonded with the barite surface*

Using the three above-mentioned methods of bare barite examination, analogous measurements were carried out for barite samples after flotation when previously coated with various amounts of TDACl (collector consumption 71.4, 142.8, 214.2, 285.6, 357 and 428.4  $\text{g t}^{-1}$ ). The coverage of 285.6  $\text{g t}^{-1}$  corresponds to a monomolecular layer of TDACl on the barite surface, when the energetic homogeneity of the surface and an area per one molecule of TDACl of  $20 \text{ \AA}^2$  were assumed.

Figure 6 presents the relationship between the amount of water bonded  $a_B$  with the barite surface and the coverage  $Z$  of the surface with TDACl determined by the quasi-isothermal method (curve 1). It appears from this figure that the amount of water bonded  $a_B$  with the surface decreases and attains a minimal value when the barite surface is covered by 285.6  $\text{g t}^{-1}$  of TDACl. There are two inflection points corresponding to 71.4 and 142.8  $\text{g t}^{-1}$  on this curve. Figure 6 also presents data determined during the dynamic adsorption of water from the gaseous phase on the relationship between the adsorption capacity  $a_A$  (maximal adsorption value) and the amount of TDACl deposited on the barite surface (curve 2). This figure indicates that the  $a_A$  value decreases linearly with the amount of TDACl deposited, and when the coverage value attains 285.6  $\text{g t}^{-1}$   $a_A$  becomes constant.

Figure 7 presents the changes of water molecules' activation energy  $\Delta E$  caused by the presence of TDACl on the barite surface. The  $\Delta E$  values were calculated from eqn. (1) on the basis of  $T$  and DTA curves from the dynamic measurements of water thermodesorption. This figure shows that water molecules have the greatest activation energy when the barite surface is covered with 142.8 and 214.2  $\text{g t}^{-1}$  of TDACl. The smallest  $\Delta E$  value is found when the barite surface is covered with 285.6  $\text{g t}^{-1}$  of TDACl. This

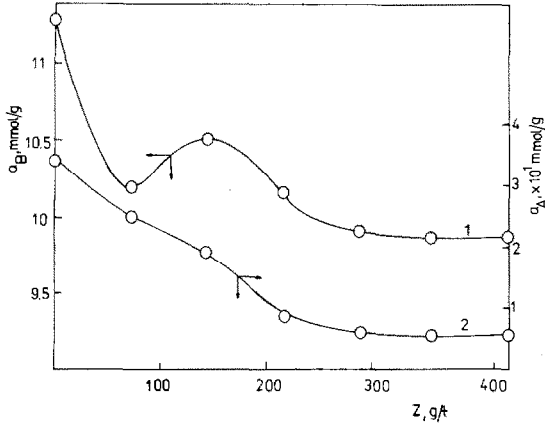


Fig. 6. Amounts of bonded water  $a_B$  and adsorbed water  $a_A$  obtained from the quasi-isothermal (curve 1) and combined (curve 2) measurements as a function of TDACl amounts deposited on the barite surface.

value is comparable with the activation energy value  $\Delta E_L$  of bulk water molecules.

Figures 8 and 9 present the changes in enthalpy  $\Delta H$  and entropy  $\Delta S$  of bonded water molecules caused by changes of the amount of TDACl deposited on the barite surface. The enthalpy and entropy changes were determined on the basis of dynamic measurements of water thermodesorption from barite samples (carried out using three values of derivatograph furnace heating rates) and on the basis of the Kissinger equations [23]

$$\Delta H = R \frac{d \cdot \ln [T_m^2 (dT_p/dt)]}{d(1/T_m)} \quad (2)$$

$$\Delta S = R \left[ \frac{\Delta H}{RT_m} + \ln \frac{\Delta H}{R} - \ln \frac{T_m^2}{dT_p/dt} - \ln \frac{kT_m}{h} \right] \quad (3)$$

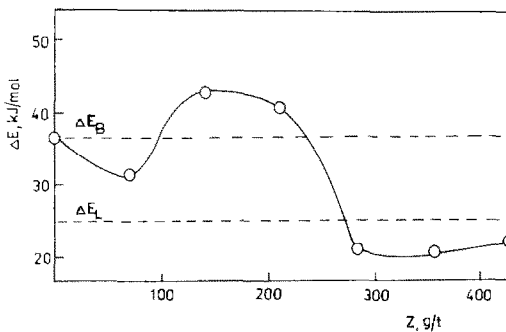


Fig. 7. The activation energies of water molecules as a function of TDACl amounts deposited on the barite surface ( $\Delta E_B$ , activation energy of bonded water on bare barite surface;  $\Delta E_L$ , activation energy of bulk liquid water).



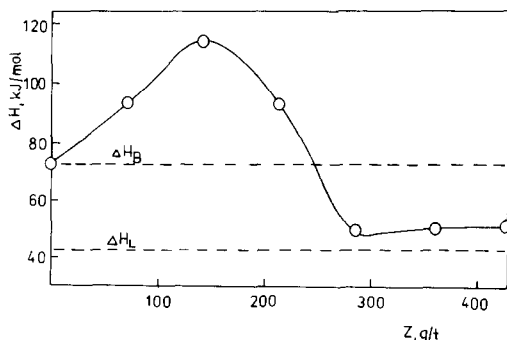


Fig. 8. The enthalpies of water evaporation from the surface as a function of TDACl amounts deposited on the barite surface ( $\Delta H_B$ , enthalpy of evaporation of bonded water from bare barite surface;  $\Delta H_L$ , enthalpy of evaporation of bulk liquid water).

where  $T_m$  is the temperature of the extreme effect point on 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.

It appears from Fig. 8 that the relationship  $\Delta H = f(Z_{TDACl})$  reached a maximum in the presence of  $142.8 \text{ g t}^{-1}$  TDACl, while a minimum is reached when the barite surface is covered with  $285.6 \text{ g t}^{-1}$  of TDACl. The enthalpy value corresponding to the minimum is  $49.96 \text{ kJ mol}^{-1}$ , and is approximately equal to the condensation heat of liquid water  $\Delta H_L = 43.89 \text{ kJ mol}^{-1}$ .

Figure 9 presents the changes in entropy  $\Delta S$  of the bonded water molecules caused by changes of the amount of TDACl on the barite surface. The relationship presented in this figure is characterized by a minimum

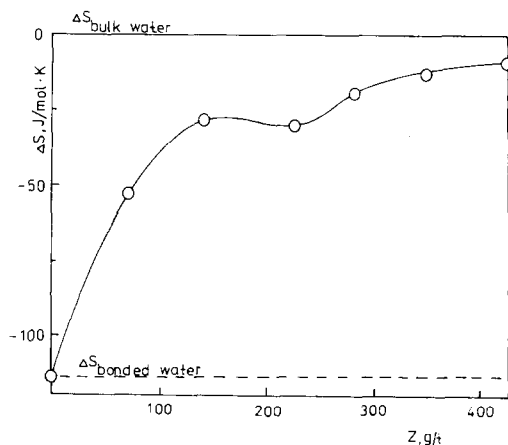


Fig. 9. The entropies of water molecules as a function of TDACl amounts deposited on the barite surface ( $\Delta S_{\text{bonded water}}$ , entropy of water molecules on bare barite surface).

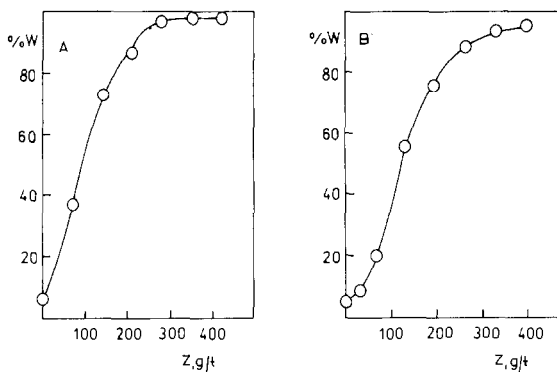


Fig. 10. Flotability of barite (% recovery) as a function of TDACl amounts deposited on the barite surface (A) and initial concentration of TDACl solution (B).

corresponding to  $214.2 \text{ g t}^{-1}$  of TDACl and by a maximum corresponding to  $285.6 \text{ g t}^{-1}$  of TDACl on the barite surface. The relationship presented in Fig. 9 is similar to those obtained for bare quartz [24] and for other mineral surfaces [4] as a function of the amount of water adsorbed.

Figure 10 presents the relationship between the percentage recovery  $W$  and the collector consumption  $Z$ . In Fig. 10A the collector layer was deposited by a solvent (methanol) evaporation but in Fig. 10B the flotability tests were performed in aqueous TDACl solution. It can be seen that flotability increases with increase of surface coverage by a collector. Flotability reaches maximal values (above 90%) for  $285.6 \text{ g t}^{-1}$  (Fig. 10A) and for  $\sim 300 \text{ g t}^{-1}$  of TDACl (Fig. 10B). These are typical flotation curves. The shape of both curves is very similar which demonstrates relatively strong adsorption of the collector from aqueous solution (i.e. its strong bonding with the barite surface). Differences in reagent consumption values became clear because some portion of the reagent remains in solution. Nevertheless the similarity of these curves allows us to presume that the model system selected in this way reflects exactly enough the real flotation system.

From Figs. 6–10 it appears that considerable changes in the investigated parameters occur in the TDACl concentration range  $0\text{--}285.6 \text{ g t}^{-1}$ . For coverages above this range these parameters are the same as at  $285.6 \text{ g t}^{-1}$ . The range from 0 to  $285.6 \text{ g t}^{-1}$  seems the most interesting, because the greatest influence of the collector on the properties of water films was found. This problem will be discussed below.

Interpretation of the changes in parameters presented in Figs. 6–9 in connection with flotation parameters requires the taking into consideration of all changes in structure, layer thickness and interaction of both TDACl and bonded water. According to present opinions, if surface coverage is less than  $285.6 \text{ g t}^{-1}$  (monolayer), TDACl is adsorbed on the barite surface by its polar part  $[\text{C}_{14}\text{H}_{29}\text{NH}_3]^+\text{Cl}^-$  (chemical interactions with polar active

sites [25]) while the hydrocarbon chain is directed outward. The dissolution of the TDACl molecules deposited on the surface in this way seems impossible. Derivatographic investigations of not-floated barite samples covered with  $285.6 \text{ g t}^{-1}$  of TDACl showed no differences in the investigated parameters in comparison with the floated sample. The results of flotation tests (Fig. 10) also suggest that dissolution does not take place (the growth in surface coverage is accompanied by the growth 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  $285.6 \text{ g t}^{-1}$  a certain solubility of these microcrystals or molecular clusters may appear. The constant flotability (Fig. 10) suggests such a possibility. Nevertheless, the aim of this paper was to examine the influence of TDACl on water properties close to the barite surface covered with the collector in the range from 0 to  $285.6 \text{ g t}^{-1}$ .

Adsorption of  $71.4 \text{ g t}^{-1}$  TDACl occurs on the most active polar centres of the barite surface. This causes the reduction of mineral surface-water interactions and in consequence a decrease of the amount of bonded water (Fig. 6) accompanied by changes in  $\Delta E$ ,  $\Delta H$  and  $\Delta S$  (Figs 7–9). Water is adsorbed on the remaining active centres of lower energy characteristics. Therefore, a water layer of structure possessing a lower intermolecular bonding energy  $\Delta E$  than that on the pure barite surface is formed (Fig. 7). They may be central pentamer type structures [16] (Fig. 4B).

The presence of  $142.8 \text{ g t}^{-1}$  TDACl on the barite surface brings about very great changes in bonded water properties. The increase of the number of hydrophobic TDACl molecules on the barite surface leads to the formation or induction of cyclic tetramer type water clusters (Fig. 4C). Water molecules contained in clusters have the greatest intermolecular bonding energy and reduced mobility (Fig. 7). Water molecules in clusters have more restricted translational and rotational motions [16], their structure is better ordered [24] and thus they have lower entropy values than those of the bulk liquid phase (Fig. 9). Destruction of such a structure requires a greater amount of energy than that at the bare barite surface (Figs. 7 and 8). The presence of hydrophobic molecules of TDACl in the vicinity of clusters of water may increase the coordinational number of water molecules up to five. Such water has a lower energetic level than water possessing a coordinational number of four in liquid water [26]. As a result the number of water molecules in the clusters situated close to the hydrophobic surface increases: this fact may be caused by the entrance of water monomers into free spaces between cluster lattices [22,27]. This suggestion may be confirmed by the greater amount of water bonded with a barite surface covered with  $142.8 \text{ g t}^{-1}$  of TDACl in comparison to that covered with  $71.4 \text{ g t}^{-1}$  of TDACl (Fig. 6, curve 1). The thickness of this water layer may be lower in comparison to that deposited on a bare barite surface because of greater condensation of molecules. That is the reason why an air bubble has easier access to the

barite surface during flotation (improvement of flotation parameters, Fig. 10).

Increase of the amount of TDACl on barite to  $285.6 \text{ g t}^{-1}$  causes complete coverage of its polar surface with the collector, and further changes in bonded water structure. The investigations carried out in our laboratory [10] showed that coverage of the barite surface with  $285.6 \text{ g t}^{-1}$  of TDACl (one statistical monolayer) leads to a decrease in the polar free surface energy from  $78 \text{ mJ m}^{-2}$  to 0 and in the dispersion one from  $66.7 \text{ mJ m}^{-2}$  to the value corresponding to the free surface energy of the hydrocarbon surface ( $25\text{--}30 \text{ mJ m}^{-2}$ ). It may be concluded that TDACl molecules adsorbed on polar sites of the barite surface also reduce dispersion interactions between the surface and water. In the barite–water system such coverage with TDACl provides a complete reduction of polar interactions and a considerable decrease in dispersion interactions between the barite surface and water. The changes in the properties of water films are very small and these properties are very similar to those in the bulk liquid phase (Figs 7–9). The TDACl layer reduces barite–water interactions and the induction of long-range water structures seems impossible. Hydrophobization of the barite surface provides the formation of water structures with characteristics similar to those of bulk water. The  $\Delta E$  value of such water molecules is  $21.74 \text{ kJ mol}^{-1}$  (Fig. 7) and indicates the formation of a cyclic trimer type structure (Fig. 4D). Water molecules' mobility is greater than the mobility of the molecules which are bonded with the bare barite surface. The entropy of these molecules is close to that of the bulk phase (Fig. 9). Then the enthalpy has a minimal value, comparable to the condensation heat of liquid water (Fig. 8). The water film formed in this manner may be called “hydrophobic” hydration [6], which appears as a result of dispersion interactions between water and the barite surface. This water film on the barite

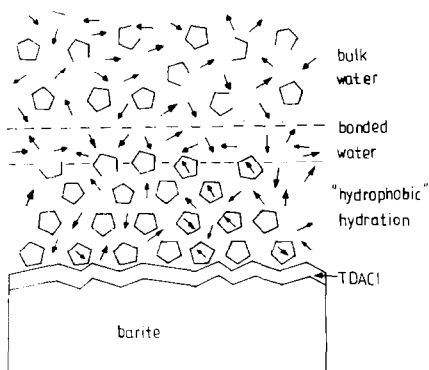


Fig. 11. The modified schematic structure of the water layer on barite with deposited TDACl (taken from Drost-Hansen [22]).

surface is unstable and has a loose structure (Fig. 11). The presence of 285.6 g t<sup>-1</sup> of TDACI on the barite surface reduces both thickness (Fig. 6) and energetic barrier of the bonded water layer; hence the facilitation of the flotation process [1-4]. When the flotation process is carried out in dynamic conditions, such a water film may be destroyed spontaneously. In these conditions an air bubble can remove the water layers and reach as far as the dry surface covered with TDACI.

## CONCLUSIONS

On the basis of our investigations, we conclude that thermodesorption of bonded water from the barite surface occurs in two steps depending on the bonding energy of the water molecules. The flotation parameters are dependent on the amount of collector deposited on the barite surface as well as on the properties of bonded water. Calculations of the thermodynamic functions showed that the main factor influencing barite flotability improvement is the significant change in the structure of bonded water caused by the presence of collector on the barite surface. The best flotability is obtained at those surface coverages by TDACI which cause the formation of loose and unstable water layers. These layers possess reduced thickness, activation energy and enthalpy as well as elevated entropy in comparison with those adsorbed on the bare barite surface. The properties of these water layers are similar to those in the bulk liquid phase as a result of the reduction of dispersion and polar interactions of the barite surface.

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