

**THERMODYNAMIC PROPERTIES AND STRUCTURE OF
WATER FILMS IN FLOTATION PROCESSES**
**Influence of adsorption of tetradecylammonium chloride
(TDAHCl) on barite and marble surfaces**

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The thermodynamic properties of water layers on barite and marble samples covered with various amounts of tetradecylammonium chloride (TDAHCl) after flotation processes were investigated by thermal analysis. The relation between the activation energy, the enthalpy and the entropy of the bonded water and the amount of TDAHCl previously deposited on the bare mineral surfaces was determined. An interpretation of the changes in these parameters, the water structure and the flotability is described.

Flotation processes take place in aqueous medium, where hydration films are present on the surface of a mineral [1]. The molecules of water in these films are ordered and strongly bonded to the hydrophilic surface of the mineral, and they result in an energetic barrier against contact between the mineral grains and air bubbles. The properties of such a hydration layer are appreciably different than those of bulk water [1-3], and this results in a different chemical potential for the water molecules [3], dependent on the film thickness.

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A hydrophilic surface coated with a certain organic reagent (collector) becomes hydrophobic, i.e. it interacts with water molecules only by dispersion forces. This is of fundamental importance as concerns flotation efficiency. The hydration layer formed on such surface possesses quite different properties, and it appears unstable ("negative disjoint pressure" [2]) when an air bubble approaches the surface. At a certain thickness, the film ruptures spontaneously and forms a "dry" area and a contact meniscus. Water in the unstable film has a raised chemical potential and vapour pressure. Such hydrophobicity, also leads to a substantial increase in the contact angle as compared with a hydrophilic surface. On the other hand, it is very difficult to investigate the hydration layers on a hydrophobic surface, and they are therefore usually studied qualitatively [3-5]. It has been stated [3] that collectors change the stability and the structure of bonded water, but the precise mechanism of these changes remains unknown.

The thickness of the bonded hydration layers and their structure, as well as the thermodynamic properties of the unstable surface layers, are also unknown. The solution of these problems would result in a better understanding of flotation processes.

In the present paper, quantitative investigations are reported on the changes in the thermodynamic properties and structure of hydration layers caused by tetradecylammonium chloride (TDAHCl) on the surface of barite and marble. The correlation of these results with flotation experimentals is also discussed.

Experimental

Natural barite and marble from mineralogical specimens were used for the measurements. The surface areas determined via the nitrogen thermodesorption chromatographic method were: barite: $0.136 \text{ m}^2/\text{g}$ (grain size $0.06\text{-}0.01 \text{ mm}$), and marble: $0.06 \text{ m}^2/\text{g}$ (grain size $0.12\text{-}0.3 \text{ mm}$).

The barite and marble samples dried at 110° were coated with TDAHCl from methanolic solution; TDAHCl is a typical collector in the flotation of quartz and barite. The minerals were coated with the collector through a method similar to that used during deposition of the stationary phase in gas chromatography [6].

The samples previously covered with TDAHCl were subjected to flotation in double-distilled water in a pneumatic apparatus for 3 min. The

nitrogen flow rate was 60 ml/min. The amounts floated out and rejected were weighed after being filtered off and dried in filter paper.

A Q-1500 D derivatograph (MOM, Hungary) was used in our investigations. The 2 g barite and 1.5 g marble samples after the flotation process

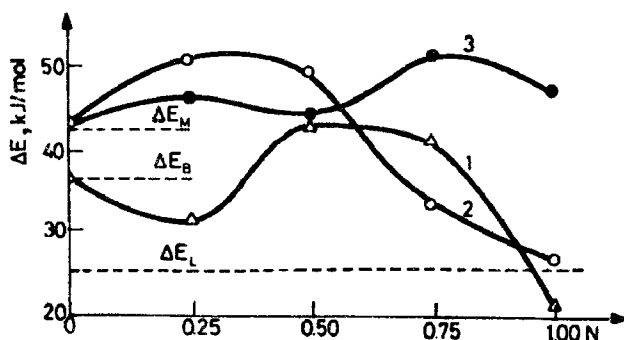


Fig. 1 The relationship between the activation energy of the water molecules and the statistical monolayer coverage of TDAHCl deposited on the barite (curve 1 - recovery samples) and marble (curve 2 - recovery samples, curve 3 - reject samples) surfaces; ΔE_B - activation energy of the bonded water on the bare marble surface, ΔE_L - activation energy of the bulk liquid water

were completely wetted with double-distilled water and then placed in a platinum crucible, and thermodesorption measurements were carried out in the temperature range 20-150°. The furnace heating rates were 0.6, 1.25 and 2.5 deg/min. The following curves were plotted: sample mass loss TG curve, differential sample mass loss DTG curve, temperature difference between the sample investigated and the standard sample DTA curve, and the temperature increase T curve. The details of the methods and the apparatus have been given previously [7, 8].

Results and discussion

Figure 1 presents the changes caused in the activation energy ΔE of the water molecules by the presence of TDAHCl on the barite (curve 1 - recovery samples) and marble (curve 2 - recovery samples, curve 3 - reject samples) surfaces. The activation energy ΔE was calculated from the Piloyan equation [9]:

$$\ln \Delta T = C - \frac{\Delta E}{RT} \quad (1)$$

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

The ΔE values were calculated on the basis of T and DTA curves from the dynamic measurements of water thermodesorption.

Figures 2 and 3 present the changes caused in the enthalpy and entropy of the bonded water molecules by changes in the amount of TDAHCl deposited on the barite (curves 1 - recovery samples) and marble (curves 2 -

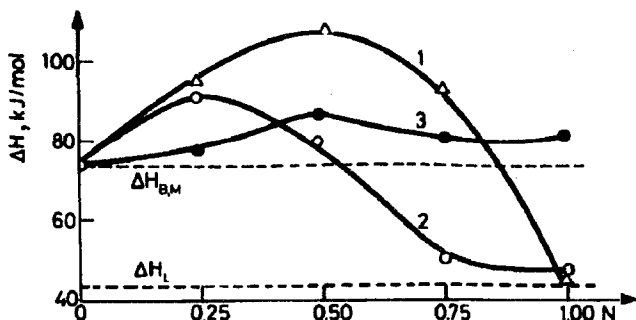


Fig. 2 The enthalpy of water evaporation from the surface as a function of the statistical TDAHCl monolayer coverage deposited on the barite (curve 1 - recovery samples) and marble (curve 2 - recovery samples, curve 3 - reject samples) surfaces; $\Delta H_{B,M}$ - enthalpy of evaporation of the bonded water from the bare barite and marble surfaces; ΔH_L - enthalpy of evaporation of bulk liquid water

recovery samples, curves 3 - reject samples) surfaces. The enthalpy and entropy changes were determined on the basis of dynamic measurements of water thermodesorption from the mineral samples (carried out at three derivatograph furnace heating rates) and on the basis of the Kissinger equations [10]:

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

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

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.

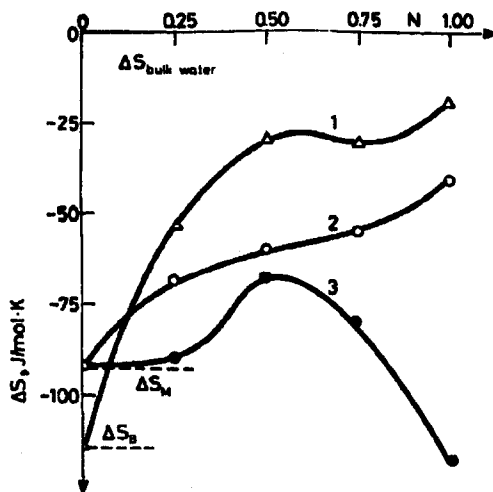


Fig. 3 The relationship between the entropy of the water molecules and the statistical monolayer coverage of TDAHCl on the barite (curve 1 - recovery samples) and marble (curve 2 - recovery samples, curve 3 - reject samples) surfaces; ΔS_B - entropy of water molecules on the bare barite surface, ΔS_M - entropy of water molecules on the bare marble surface, $\Delta S_{\text{bulk,water}}$ - entropy of liquid water molecules

Figure 4A shows the dependence of the percentage recovery W on the number of statistical TDAHCl monolayers N , and Fig. 4B the dependence on the concentration C (curves 1 - barite, curves 2 - marble). From this Figure, it can be seen that the flotability increases with increase of the surface coverage with the collector (Fig. 4A) and with increase of the collector concentration (Fig. 4B). The flotability reaches a maximum value (above 90% - barite, and 86% - marble) for 1 TDAHCl monolayer and for 8 mg/l of TDAHCl. These are typical flotation curves, which demonstrate the relatively strong adsorption of the collector from aqueous solution (its strong bonding with the barite and marble surfaces). It is currently considered [7, 8] that, if the surface coverage is less than 1 monolayer, TDAHCl, $[\text{C}_{14}\text{H}_{29}\text{NH}_3]^+\text{Cl}^-$ is adsorbed on the barite and marble surfaces by its polar part (chemical interactions with polar active sites), while the hydrocarbon chain is directed outwards. At higher coverages, microcrystals

or molecular clusters possessing properties similar to those of solid TDAHCl can be formed.

Adsorption of the first portions of TDAHCl occurs on the most active centres of the barite and marble surfaces. The water molecules adsorbed on these active centres of the bare barite and marble samples are most strongly

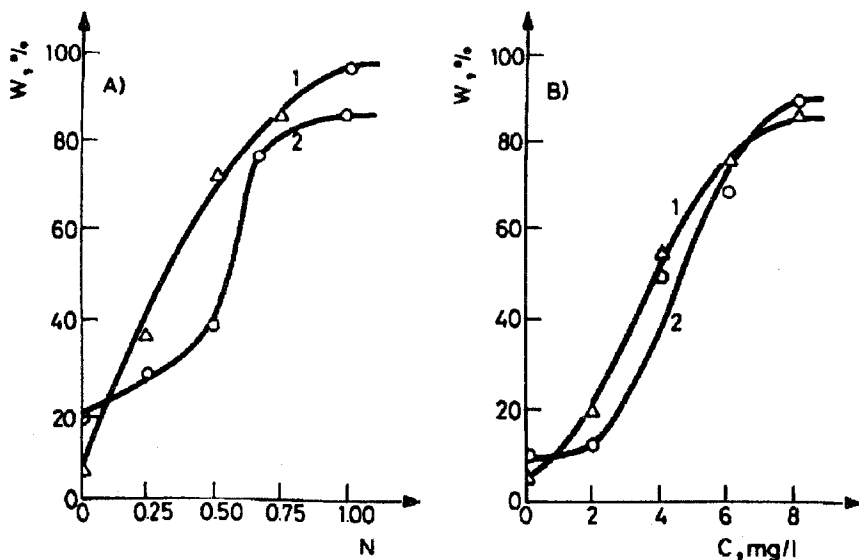


Fig. 4 The flotability (% recovery) of barite (curves 1) and marble (curves 2) as a function of the TDAHCl amount deposited on the surfaces (A) and the initial concentration of the TDAHCl solution (B)

bonded to the mineral surfaces. The ΔE values calculated from Eq. 1 for the water molecules on the bare barite and marble surfaces are $\Delta E_B = 36.8$ kJ/mol and $\Delta E_M = 42$ kJ/mol, respectively (Fig. 1). These values are higher than that needed for the destruction of hydrogen-bonds in bulk water ($\Delta E_L = 25.08$ kJ/mol). From a comparison of the experimentally determined ΔE_L values and those calculated on the basis of quantum mechanics by Klier and Zettlemyer [11], it results that water structures of the pentamer type (Fig. 5A) may exist on bare barite, and structures of cyclic type (Fig. 5C) on bare marble surfaces. These aggregates with four hydrogen-bonds are most compact and ordered ones (the minimal entropy value $\Delta S_B = -117.1$ J/mol deg, $\Delta S_M = -92$ J/mol deg, see Fig. 3). Such an adsorption mechanism results from both dispersion and polar interactions between the water molecules and the barite and marble surfaces (water: $\gamma_W^d = 21.8$ and $\gamma_W^p = 51$ mJ/m²,

barite: $\gamma_B^d = 66.7$ and $\gamma_B^p = 78$ mJ/m², and marble $\gamma_M^d = 67$ and $\gamma_M^p = 101$ mJ/m²) and the fact that the energetically-preferred process is aggregate formation rather than the formation of single hydrogen-bonds [1, 2, 11] (the hydrogen-bond energy is 25.08 kJ/mol and the condensation heat is 43.89 kJ/mol). Evaporation of these water molecules from mineral surfaces requires the greatest amount of energy [7, 8].

The adsorption of TDAHCl on the barite and marble surfaces results in considerable changes in the water film properties on these surfaces. The amount of adsorbed and bonded water is significantly smaller [7, 8]. As can

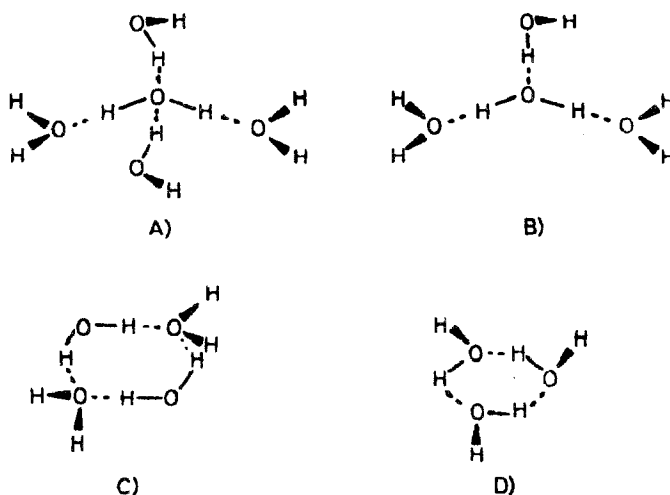


Fig. 5 Geometry of some water clusters (taken from Klier and Zettlemoyer [11]): A - pentamer (-33.1 kJ/mol), B - central tetramer (-30.35 kJ/mol), C - cyclic tetramer (-43.89 to -17.97 kJ/mol), D - cyclic trimer (-23.4 to -8.8 kJ/mol)

be seen from Figs 1-3, the dependences $\Delta E = f(N)$, $\Delta H = f(N)$ and $\Delta S = f(N)$ are polyextremal. This suggests that changes occur in the structure of the water film adsorbed on the mineral surfaces modified with various amounts of TDAHCl. The adsorption of 1 TDAHCl monolayer on the barite and marble surfaces (recovery samples) probably causes a complete coverage of its polar surface with the collector. Our earlier investigations [12] showed that coverage of the barite and marble surfaces with 1 monolayer of TDAHCl leads to a decrease in the polar components of the surface free energy γ_S^p to 0 and to a decrease in the dispersion components

γ_s^d to the values corresponding to the surface free energy of the hydrocarbon surface (25-30 mJ/m²). Thus, the TDAHCl molecules adsorbed on the polar sites of the barite and marble surfaces provide a complete reduction of the polar interactions and also reduce the dispersion interaction between the surface and the water. The thermodynamic properties of these films adsorbed on the recovery samples of the investigated minerals are very similar to those in the bulk liquid phase (Figs 1-3, curves 1 and 2). The TDAHCl molecules reduce the surface-water interactions, and the induction of long-range water structures seems impossible. The adsorption of the TDAHCl monolayer on the barite and marble surfaces (recovery samples) allows the formation of a water structure with characteristics similar to those of bulk water. The ΔE values of such water molecules are 21.74 kJ/mol (barite - Fig. 1, curve 1) and 26.5 kJ/mol (marble - Fig. 1, curve 2), and they indicate the formation of a cyclic trimer or central tetramer type structure with three hydrogen-bonds in the clusters (Fig. 5B, D).

The entropies of these molecules (Fig. 3, curves 1 and 2) are between the entropies of the bonded (ΔS_B , ΔS_M) and bulk water, and this indicates that the mobility of the water molecules is greater than the mobility of the molecules bonded to the bare mineral surfaces. The enthalpy then has a minimum value (Fig. 2, curves 1 and 2) comparable to the condensation heat of liquid water ΔH_L . The water film formed in this manner may be called "hydrophobic" hydration, which appears as a result of dispersion interactions between the water and the mineral surfaces covered with TDAHCl. This water film on the barite and marble surfaces (recovery samples) is unstable and has a loose structure in comparison with that for the bare surfaces (calculated critical film thickness on marble surface $h = 23.1$ nm) [8]. The presence of 1 TDAHCl monolayer on the barite and marble surfaces (recovery samples) reduces both the thickness [7, 8] and the energetic barrier of the bonded water layer, and this facilitates the flotation process. When the flotation process is carried out under dynamic conditions, such a water film may be destroyed spontaneously. Under these conditions, an air bubble can remove the water layers and reach as far as the dry surfaces covered with TDAHCl.

From Figs 1-3, curves 3, it appears that the changes in the properties of the water layers on the marble surface of the reject samples are almost the same as those on the bare marble surface. The marble surface is a heterogeneous one and the separate grains do not seem equivalent in their surface properties. Thus, the deposited TDAHCl layer is probably not

uniform in thickness. Therefore, almost no influence of the collector layer on the surface water layers was observed for the reject samples.

Conclusion

The above results and calculations demonstrate the considerable changes in the thermodynamic properties and structure of the hydration layers affected by the long-chain collector adsorbed on barite and marble surfaces. These properties appear to be strongly dependent on the amount of collector adsorbed. On the bare surface of minerals, the water molecules are strongly bonded and ordered, and the structure of the hydration layers is quite different from that in bulk water. This results from both dispersion and polar interactions between the water molecules and such surfaces. Collectors provide a decrease in dispersion interaction of the mineral surface and a complete reduction of polar ones, and therefore the thermodynamic properties of the hydration layers change significantly. They appear similar to those of bulk water: the ice-like structures with four hydrogen-bonds formed on bare surfaces are transformed to these from bulk water possessing three hydrogen-bonds. Such hydration layers may be disrupted spontaneously when an air bubble approaches a mineral surfaces. It seems possible to generalize the above conclusions for other mineral-collector systems.

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Zusammenfassung - Mittels Thermoanalyse wurden nach Schwimmaufbereitungsverfahren die thermodynamischen Eigenschaften der Wasserschichten über Baryt- und Marmorproben mit verschiedenem Gehalt an Tetradecylammoniumchlorid (TDACI) untersucht. Es wurde die Beziehung zwischen der Aktivierungsenergie, der Enthalpie und der Entropie

des gebundenen Wassers und der Menge an zuvor an der Oberfläche des bloßen Minerals festgesetzten TDACI festgestellt. Die Veränderlichkeit dieser Parameter sowie die Bindung des Wassers und die Flotierbarkeit werden interpretiert.