

## Adsorption of cetyltrimethylammonium bromide on parent and molybdenum-modified silica gels in the solid state

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### Abstract

The adsorption of the cationic surfactant cetyltrimethylammonium bromide (CTAB) on silica gel and on molybdenum-modified silica gel substrate, in the solid state, was studied by differential scanning calorimetry and Fourier transform IR photoacoustic spectroscopy (FTIR-PA) techniques.

Examination of the solid state IR spectra of CTAB absorbed onto molybdenum-silica substrate, as a function of temperature, shows a new band at  $938\text{ cm}^{-1}$  shifted to  $961\text{ cm}^{-1}$  (during the temperature flow), representing a chemisorption via the interaction of the head group of the surfactant  $(\text{CH}_3)_3\text{N}^+$  and  $\text{Mo}=\text{O}$  stretching vibration species.

In the presence of NaCl, shifting of the high temperature exothermic peak at  $411^\circ\text{C}$  to  $451^\circ\text{C}$  was obtained, providing an enhancement of cetyltrimethylammonium chloride adsorption onto molybdenum-silica substrate and a considerable reduction in the  $\Delta H$  value is observed. This decrease in the  $\Delta H$  value was obtained as a result of the interference of the less reactive site  $\text{Na}^+$  ions in the adsorption, because of substitution of  $\text{Na}^+$  for  $\text{Mo}^{6+}$  ions.

### INTRODUCTION

The adsorption of cetyltrimethylammonium bromide (CTAB) on silica in aqueous and non-aqueous media has been extensively studied over the last two decades [1–3].

The behaviour of the adsorption of CTAB on silica and on metal rod surfaces, from solutions, have been evaluated using Fourier transform IR (FTIR) and surface enhanced Raman spectroscopy techniques [4–5].

Calorimetric measurements concerning the adsorption of surfactants on silica gel from solutions have recently been described [6, 7].

Fewer studies have been reported on metal-surfactant complexes.

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However, detailed information concerning the adsorption of cationic surfactant on silica substrate modified by metal ions has not yet been carried out.

As stated by Ikeda and co-workers [8], surfactants in aqueous solutions generally form spherical micelles above certain critical concentrations, and some other surfactants (i.e. ionic ones) can form rod-like micelles over a certain range of concentration of surfactant or added electrolyte.

The sphere–rod transition has been deduced from physical measurements of viscosity, conductivity and flexibility of rod-like micelles [9, 10].

In this paper, the adsorption of CTAB on molybdenum-modified silica gel substrate with time and the influence of temperature using DSC and FTIR-PA have been investigated and discussed. Moreover, the effect of NaCl addition on the properties of the modified substrate is also examined.

## EXPERIMENTAL

### *Materials*

Silica gel 60 (Merck) with a particle size of 0.040–0.063 mm (230–400 mesh ASTM) was used as a support.

The molybdenum-loaded sample (10 wt.% with a surface area of  $250 \text{ m}^2 \text{ g}^{-1}$ ) was prepared by impregnation with an aqueous solution of ammonium heptamolybdate  $(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ .

The Mo-modified substrate was dried at 393 K and finally calcined at 773 K in air for 16 h.

$5 \times 10^{-3} \text{ M}$  CTAB (Aldrich) was used to study its adsorption onto Mo-modified silica gel substrate.

The surfactant concentration was chosen to be above the CTBA critical micelle concentration (CMC), which is known to be  $9 \times 10^{-4} \text{ M}$  [11], to prevent any change in the adsorption as a result of the surfactant concentration.

0.5 M NaCl (AR) was also used to prepare  $5 \times 10^{-3} \text{ M}$  CTAB in order to estimate the influence of the electrolyte on the micelle and consequently on the samples under investigation.

### *Adsorption of CTAB on the samples*

Twenty milliliters of CTAB was mixed with 0.16 g of the sample (silica or Mo-silica) in a stoppered centrifuge tube, and the mixture was gently stirred by a magnetic chip for the required time at 25°C.

The sample suspensions were centrifuged at 3000 g to sediment the sample, and the supernatant was carefully withdrawn. The sedimented samples were dried at 393 K for 4 h and placed in a dry nitrogen-purged glovebox.

### Characterization of the samples

For DSC measurements, 12 mg of the sample was taken in Al crucibles and treated in a Perkin-Elmer DSC7 unit and scanned from 30 to 500°C at a rate of 10°C min<sup>-1</sup>. Al metal was used as a reference and a nitrogen purge of 50 ml min<sup>-1</sup> was used during the experiment.

IR spectra were recorded with a Nicolet 5-DXB FTIR spectrometer, using a METC-100 photoacoustic detector.

In this work, a scan speed of 0.16 cm s<sup>-1</sup> was used. This gives the strongest photoacoustic signals. The spectra were taken with 4 cm<sup>-1</sup> resolution and 300–500 scans were averaged, depending on the intensity of the signal.

### RESULTS AND DISCUSSION

The DSC thermograms of the parent silica gel 60 calcined at 773 K, silica gel 60 modified with 10 wt.% Mo and silica gel 60 with 0.005 M CTAB are shown in Fig. 1.

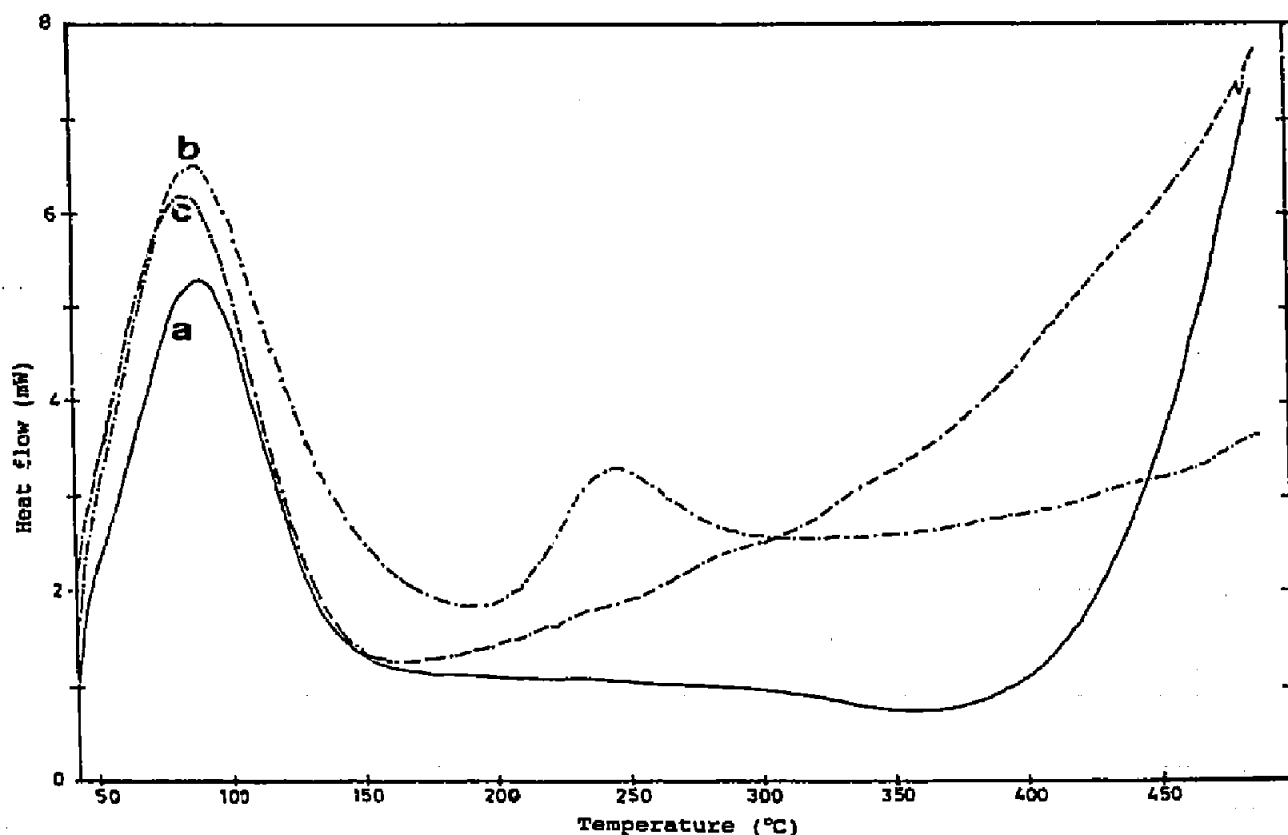


Fig. 1. DSC thermograms: curve a, silica gel 60, calcined at 773 K; curve b, silica gel 60 modified with 10 wt.% Mo, calcined at 773 K; curve c, silica gel 60 + 0.0005 M CTAB, heated at 373 K.

An exothermic peak with a maximum at 89°C for the parent sample is observed. The same peak position is also observed for the Mo-modified silica gel sample, but with another exothermic peak at 242°C.

In the case of the silica gel 60 plus CTAB system, a large exothermic peak around 87°C is obtained.

Therefore, it is noteworthy that the first exothermic peaks (low temperature peak) in all the samples have the same peak position but differ only in  $\Delta H$  values. The increase in  $\Delta H$  intensity of the low temperature peak for the silica gel 60 plus CTAB system indicates a value of 102 J g<sup>-1</sup>, whereas silica gel 60 modified with 10 wt.% Mo and the parent sample give values of 99 and 66 J g<sup>-1</sup> respectively.

However, we may attribute this difference to the involvement of the water which could have been obtained during the preparation.

The second peak observed for the Mo-silica sample represents possible interactions between molybdenum and silica, Mo replacing a considerable number of hydroxyl groups, indicating the high probability of oxygen vacancies; polymolybdate species could be obtained. This peak gives a  $\Delta H$  value of 16.6 J g<sup>-1</sup>.

According to the findings of Cirillo et al. [12], large areas of alumina surface remain uncovered at 8 wt.% Mo loading, and because we need to reach to a fairly uniform distribution of Mo over a large surface area of silica gel, we tried to cover our surface with a 10 wt.% Mo loading.

Furthermore, Fig. 1 also indicates that there is no interaction between the parent sample and the surfactant CTAB, revealing that no bond formation could be obtained during the temperature flow.

Figure 2 shows the DSC scans of the influence of time on the adsorption of CTAB on silica gel 60 containing 10 wt.% Mo. Two exothermic peaks with maxima at 78–80 and 411°C were observed throughout thermograms a–e in Fig. 2. It is observed that the first temperature peak is shifted to a lower temperature than for silica gel modified with 10 wt.% Mo (Fig. 1).

Moreover, the intensity of the peak becomes smaller after CTAB adsorption takes place. It is obvious that CTAB has a considerable influence on the low temperature peak, representing the interaction with the rest of the non-reacted hydroxyl groups and indicating that the presence of molybdenum helps CTAB adsorption.

Furthermore, a decrease of the  $\Delta H$  values for the low temperature peaks was observed with time.

It was found also that the  $\Delta H$  values for the exothermic peaks at 411°C increase continuously with time to give values of 46.3, 131.9 and 149.9 J g<sup>-1</sup> at 10, 20 and 60 min respectively, and then decrease after 180 and 400 min to give  $\Delta H$  values of 111.3 and 112.0 J g<sup>-1</sup> respectively. This can be due to such a high Mo loading: an excess of MoO<sub>3</sub> can aggregate to form a bulk phase on the surface, blocking off the pores of the silica with Mo. At such a

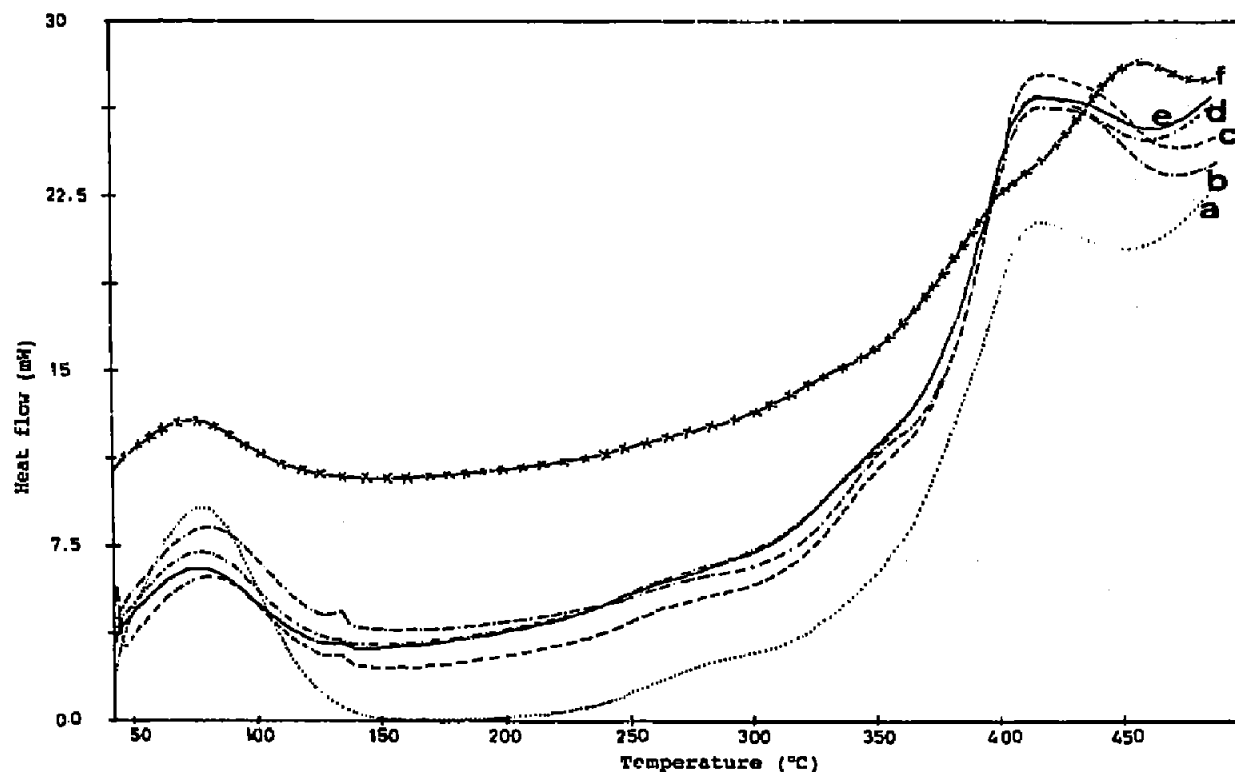


Fig. 2. DSC thermograms of CTAB adsorbed on silica gel 60 modified with 10 wt.% Mo as a function of time: curve a, 10 min; curve b, 20 min; curve c, 60 min; curve d, 180 min; curve e, 400 min. Curve f shows the influence of 0.5 M NaCl on the modified sample.

high coverage of CTAB (correlated with time) the less reactive sites are occupied and consequently  $\Delta H$  decreases.

The activation energy values (which are valuable data attributed to the relative values of various properties of the various active sites present in the solid materials under study and the strength of their interactions) have almost identical  $E_A$  values. It is clear from Table 1 that after 20 min

TABLE 1

Parameters of the high temperature peaks (411 and 451°C) obtained from CTAB adsorbed onto Mo-silica substrate by DSC as a function of time

Time (min)	Temp. range (°C)	Peak max. (°C)	$\Delta H$ (J g <sup>-1</sup> )	$E_A$ (kJ mol <sup>-1</sup> )
10	365–455	411	46.3	44.7
20	370–471	411	131.9	53.9
60	368–470	411	149.9	53.7
180	370–461	411	111.3	51.4
400	372–460	411	112.0	50.1
20 <sup>a</sup>	426–478	451	34.1	40.3

<sup>a</sup> Data based on the result of interaction of Mo-silica sample with CTAB dissolved in 0.5 M NaCl.

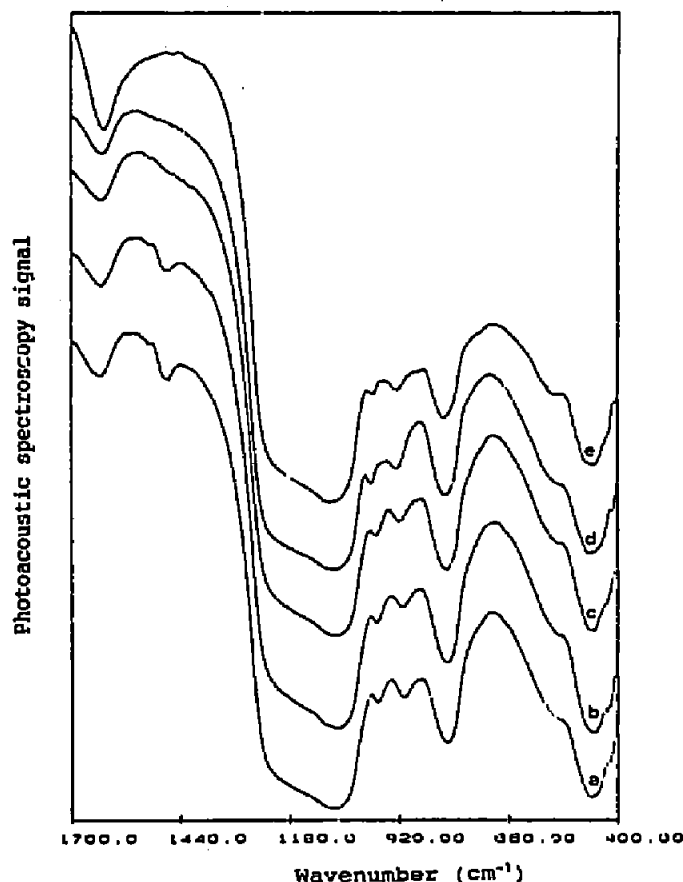


Fig. 3. Low frequency FITR-PA spectra of CTAB adsorbed onto 10 wt.% Mo-silica sample, as a function of the temperature flow. Samples represented by curves a, b, c, d and e were desorbed at 413, 473, 543, 643 and 723 K respectively.

adsorption is being limited and no more room is available on the adsorbent for further molecules to be adsorbed. Therefore, a decrease in  $E_A$  with time is obtained.

The peak at 242°C (from Mo-silica interaction) completely disappears upon CTAB adsorption and the prominence of the new peak at 411°C reflects a major interaction of Mo with CTAB. The above result is consistent with the IR spectra taken for the Mo-modified silica sample at various temperatures (Fig. 3).

Figure 3 shows (in the range 1700–400  $\text{cm}^{-1}$ ) a new band at 938  $\text{cm}^{-1}$  and three other bands at 986, 867 and 694  $\text{cm}^{-1}$ , representing the silica structure. At the beginning, the band at 938  $\text{cm}^{-1}$  is attributable to the involvement of water, but on heating the sample to 723 K the prominence of this band suggests chemical bond formation.

This is supported by the shifting of the band at 938  $\text{cm}^{-1}$  with a continuous increase in temperature (to 723 K) to 961  $\text{cm}^{-1}$ .

From the above discussion, it is obvious that this band at 938  $\text{cm}^{-1}$  is a result of a preferential interaction of Mo with CTAB. Therefore, it is

reasonable to assign the  $938\text{ cm}^{-1}$  band to the stretching vibrations of  $\text{Mo}=\text{O}\cdots\text{N}^+\text{C}$  mode.

The  $\text{MoO}_3$  species is formed preferentially at such a high wt.% of molybdenum and therefore the terminal  $\text{Mo}=\text{O}$  species is obtained. Moreover, IR data shows that no band is formed in the place of that at  $938\text{ cm}^{-1}$  between silica gel and CTAB, which supports our assignment.

Therefore, it is reasonable to correlate the thermogram peak at  $411^\circ\text{C}$  to the chemical bond  $\text{Mo}=\text{O}\cdots\text{N}^+\text{C}$  obtained from IR data. Figure 2f shows the effect of NaCl addition on CTAB adsorption. Two exothermic peaks at  $74$  and  $451^\circ\text{C}$  were observed. This thermogram clearly reflects a major change if it is compared to the others. The shift of the high temperature peak from  $411$  to  $451^\circ\text{C}$  reflects the strength of the  $\text{Mo}=\text{O}\cdots\text{N}^+\text{C}$  bond upon electrolyte addition.

Ikeda and co-workers [8] showed that for a series of cationic surfactants in NaCl solutions a sharp break in the apparent micelle molecular weight is observed when the salt concentration reaches a value of  $0.45\text{ M}$ , which corresponds to the sphere–rod transition. Therefore, in our case the driving force could be referred to the change of the structure when the small  $\text{Cl}^+$  ions replace the larger  $\text{Br}^-$  ions causes an enhancement of  $\text{CTA}^+$  affinity towards  $\text{Mo}=\text{O}$  species.

Accordingly, the increase of interaction of cetyltrimethylammonium chloride (CARC) and Mo causes a decrease of the  $\Delta H$  value.

It is likely to assume that the strong interaction between Mo and  $\text{N}^+\text{C}$  will initiate further reaction of successive amounts of CTAC, so the less reactive site  $\text{Na}^+$  ions (originating from the high concentration of the NaCl electrolyte used) will interfere with such interaction and consequently  $\Delta H$  will decrease. Mo ions impregnated on silica can expose  $\text{Mo}=\text{O}$  species on the surface to enhance the  $\Delta H$  value upon adsorption. However, the heterogenous surface site distribution obtained as a result of the replacement of Mo ions by less active  $\text{Na}^+$  ions causes the significant decrease of both  $\Delta H$  and  $E_A$  values.

The low temperature peak of the same thermogram (Fig. 2f) also shows the involvement of  $\text{Na}^+$  ions in the hydroxyl groups region by shifting the peak to a lower temperature of  $74^\circ\text{C}$  compared to the others.

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