

Adsorption properties of ionic surfactants on molybdenum-modified silica gels

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Abstract

The adsorption of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) surfactants on silica gel has been measured as a function of added molybdenum and NaCl by volumetric isotherms (from solution) as well as Fourier-transform IR spectroscopy (FTIR-PA), in the solid state. The adsorption of both surfactants onto molybdenum-modified silica surfaces shows two phase transitions, whereas only one phase is obtained upon the adsorption of these surfactants onto the parent silica.

CTAB shows a significant increase upon adsorption onto molybdenum-modified silica compared with SDS especially following the addition of NaCl (0.5M), due to the evolution of MoO₃ species following calcination, the high degree of CTAB structure change with the addition of NaCl, and the lower degree of interference of Cl⁻ and CTA⁺ ions than that of SD⁻ ions.

The volumetric isotherms were shown to be a good tool for elucidating the adsorption mechanism. The IR spectra of CTAB adsorbed onto the molybdenum-silica system in the hydroxyl group region, at the extent of the electrolyte concentration, showed that adsorption occurs mainly via H-bonded silanols owing to steric crowding might be obtained at increasing electrolyte concentrations, which prevent the terminal hydroxyl groups from reacting properly, and the relatively long alkyl chain of CTAB compared with that of SDS.

Keywords: Adsorption; CTAB; FTIR; Mo/SiO₂ catalyst; SDS; Volumetric analysis

1. Introduction

It is well known that addition of electrolytes to surfactant solutions causes changes in the size, shape, polydispersity and the flexibility of ionic micelles [1–4]. Under the influence of electrolytes, especially at threshold concentrations, it has been found that the micelles undergo a change from spheres to cylinders [1,5,6]. In view of the importance of this sphere-to-rod transition, from both theoretical and practical points of view [1–3], many interactions in aqueous solutions have been studied [1–6]. In contrast, few studies have been

reported on surfactant interactions in the solid state [7].

Because of the geometrical and structural arrangement of silica gel, many authors have studied the adsorption of ionic surfactants onto silica surfaces in aqueous or non-aqueous solutions [8–10]. Recently, silica gel modified with organic groups has been used to adsorb metal ions from non-aqueous solutions in order to separate such ions [11–12]. Micelles have also been used in catalysis, especially in homogeneous interactions (e.g. liquid-liquid [13,14]), while work on heterogeneous interactions, on which a vast majority

of industrial processes depend, a lot of effort is still required. Accordingly, heterogeneous systems employing surfactants should be studied in order to follow the important features of this system, such as the rates, energetics of adsorption, structure of the active surface, and the transition accompanying the surfactant.

Therefore, the aim of this paper is to follow the adsorption of CTAB and SDS surfactants on silica gel modified with molybdenum catalyst through the adsorption isotherms and the FTIR-PA technique. However, no attempts have been made to investigate the adsorption of such ionic micelles, and their states following the addition of electrolytes to silica–molybdenum catalyst in the solid state.

2. Experimental

Silica gel 60 (Merck) with a particle size of 0.040–0.063 mm (230–400 mesh ASTM) and a surface area of $450 \text{ m}^2 \text{ g}^{-1}$ was used as a support. The molybdenum-loaded silica sample (9 wt.%) with which a fairly uniform distribution of the Mo on the large surface area silica can be obtained, 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 sample was dried at 393 K and finally calcined at 773 K, in air, for 16 h.

CTAB and SDS (Aldrich) were used to study their adsorption onto Mo-modified silica catalyst. NaCl (AR) was also used to estimate its influence on the adsorption behaviour. The adsorption isotherms were carried out at a temperature of 25°C , higher than the Krafft points of the used surfactants. About 1 g of the Mo-modified silica was equilibrated with CTAB or SDS at concentrations higher than the CMC. The pH values were adjusted to 8 for CTAB and 4 for SDS in order to obtain the maximum adsorption values.

The amount of surfactant adsorbed by the substrates was calculated using the equation

$$N_f = (N_a - N_s)/W,$$

where N_f is the amount of the surfactant adsorbed per gram of the solid phase. The amounts of surfactant adsorbed (SDS and CTAB) were deter-

mined, after the system had reached equilibrium, by taking the supernatant and applying the previously cited methods configured for these surfactants [15–16]. N_a is the amount (in moles) of the surfactant in solution before adding to the solid phase, N_s is the amount (in moles) of the surfactant in solution in equilibrium with the solid phase, and W is the mass of the solid. The precipitates were dried at 393 K for 4 h and placed in a dry nitrogen-purged glovebox enclosing the photoacoustic cell (PA) into which the appropriate sample was placed, and then transferred into the FT equipment. The PA spectra were recorded on a Nicolet 5-DXB-FTIR spectrometer. More details of the IR instrument can be found elsewhere [17,18].

3. Results and discussion

3.1. Adsorption isotherms

Fig. 1 shows the volumetric isotherms of CTAB and SDS adsorption at 25°C for silica and Mo-modified silica catalyst. As shown in Fig. 1, the isotherms attained constant maximum values since the concentrations used were greater than the estimated CMCs for the two surfactants.

For CTA^+ and SD^- , no steps in the isotherms can be observed for the non-modified silica, as have been found for other types of silica [8,15]. This could be attributed to the homogeneity of the silica surface used here. However, the adsorption of both surfactants onto Mo-modified silica reflect two phase transitions.

The adsorption isotherm of CTA^+ on silica, at

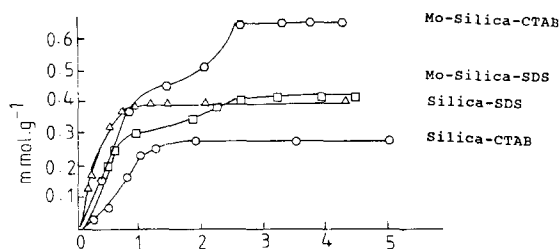


Fig. 1. Adsorption isotherm of CTA^+ (at $\text{pH}=8$) and SD^- (at $\text{pH}=4$) on silica and Mo-silica catalysts.

pH 8, was more or less similar to those observed in previous works. However, a significant increase in the CTA^+ adsorption onto Mo–silica catalyst was observed compared with the corresponding SD^- surfactant, which showed a significant decrease especially for the first plateau if it is compared with the SD^- adsorbed on the non-modified silica.

The adsorption of CTA^+ ions onto Mo–silica catalyst is greatly enhanced compared with SD^- ions because of the reversed charge that could have been obtained upon impregnating the silica catalyst with Mo. This could be achieved through impregnating silica with Mo followed by calcination to create new active centres (MoO_3 , Mo-OH and Mo-O-Mo) capable of enhancing CTA^+ adsorption [19] to a second phase transition.

The existence of two phase transitions in the adsorption of SD^- onto Mo–silica and the significant decrease observed for the first plateau indicates the involvement of the Mo catalyst, which covers the majority of the silica surface by negative charges. Furthermore, the presence of Mo(VI) on the silica surface reduces the surface charge density of the substrate and consequently reduces the attraction force between SD^- and silica–Mo; as a result the degree of ionization of SDS is decreased. More interestingly, the higher density of the sulphate group (SDS) upon adsorption than that of Br^- (CTAB) might lead to the expected low binding when SD^- comes to interact. These conclusions confirm that the impregnation of silica with Mo catalyst creates a surface heterogeneity phenomenon [20] that is responsible for enhancing the adsorption of the ionic surfactants to a second plateau.

Most probably the charge neutralization mechanism [8] operates in this system; this can be explained as follows. Impregnating silica with Mo at such high wt.%, followed by calcination, forms MoO_3 as a bulk layer. However, when adding the CTA^+ surfactant to this system, one would expect that CTA^+ will take place on the negative part of the silica surface, obtained as a result of the pH effect. This is evidenced by the similarity between the first plateau obtained from silica and that obtained from silica–Mo. The heterogeneity of the surface, especially those formed from MoO_3 , will

enhance the adsorption of CTA^+ to further sites to build up the second plateau.

Since the difference between the second and first plateaus in Mo–silica catalysts is not equal to the height of the first plateau, a bilayer model cannot be expected from these experiments. The effect of added NaCl upon the adsorption of SDS and CTAB ions can be clearly seen in Fig. 2. It seems that the addition of NaCl has a much greater effect on enhancing the adsorption.

The interpretation of the increased adsorption for ionic surfactants containing more than one counterion is, of course, an oversimplification since it is hard to take into account the effects of the ionic strength, viscosity, exchange capacity and the effect of the cation (Mo) on the CMCs of the two surfactants. Therefore, for simplicity, the isotherms of Fig. 1 are compared with those in Fig. 2 in order to reveal the influence of the addition of NaCl (0.5M). The increase in adsorption with NaCl can be attributed to the transition from spheroidal aggregates to rod-like structures with much lower surface areas and more flexibility, i.e. an acceleration and enhancement of ion adsorption is accomplished.

It is clear from Fig. 2 that there is no difference in the nature of the isotherms from those in Fig. 1 with the addition of salt. Furthermore, the appearance of the plateaus at similar equilibrium concentrations can also be seen. It is obvious that the

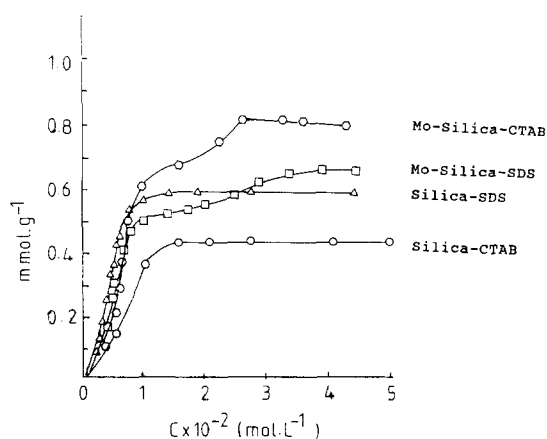


Fig. 2. Adsorption isotherm of CTA^+ (at pH=8) and SD^- (at pH=4), in the presence of 0.5M NaCl, on silica and Mo–silica catalysts.

presence of salt increases the amount of adsorbed surfactant and the level of the isotherm plateau. By adding the electrolyte the absorption was found to be enhanced by a factor of around 2.0.

The addition of Na^+ counterions enhanced the adsorption of the ionic surfactants but did not alter the nature of the isotherms or the transition steps, according to the results of Bunton et al. [21]. They found that the ionic exchange constant for Na^+ in ionic micelles is practically around the value of one. This means that such an electrolyte can enhance the surfactant adsorption according to the established change in size and morphology within the same range of the transition step, i.e. the electrolyte does not give a distinct transition.

3.2. Hydrogen bonding considerations and surface hydroxyl groups

It has been shown that a significant increase in the absorption of cationic surfactant is highly dependent on the presence of molybdenum. This result is also reflected in the IR spectra, in the solid state, by enhancing the intensity of the C–H bands in the 2800–3000 cm^{-1} region for CTAB on ammonium heptamolybdate (previously calcined at 773 K for 6 h) compared with that of SDS (Fig. 3) surfactant.

In order to differentiate between the adsorption of CTAB on silica and on Mo–silica catalysts, the estimated influence of hydrogen bonding on the structural aspects of silica gel is clarified in Fig. 4. The free OH band at 3749 cm^{-1} is significantly reduced in the case of modified silica upon CTAB adsorption compared with the non-modified sample. In the IR spectrum of silica–CTAB this band is preceded by two bands at 3660 and 3551 cm^{-1} due to H-bonded silanols.

With the addition of Mo, a feature at 3720 cm^{-1} is observed with a barely discernible band at 3660 cm^{-1} ; this can be attributed to silanols weakly perturbed via H-bonding (being not too near to each other) [22]. The small band at 3720 cm^{-1} indicates that very few terminal H-bonded OH groups are present. Furthermore, the broadness of the 3551 cm^{-1} band upon the addition of molybdenum reflects the accessibility of the vicinal silanol for H-bonding. The decrease

in the intensity of the band at 3749 cm^{-1} and the virtual disappearance of the 3660 cm^{-1} band in the modified silica–CTAB spectrum relative to the increase in the 3551 cm^{-1} band suggests a higher degree of perturbation of the isolated silanols via H-bonding. The barely visible small band at 3660 cm^{-1} in the modified silica–CTAB spectrum indicates that part of the surface still shows weakly perturbed H-bonds (lateral interaction).

Figs. 5 and 6 reveal the influence of the addition of electrolyte on the adsorption of SDS onto silica and silica–Mo catalyst in the solid state. Fig. 5 shows the progressive growth of the C–H stretching modes in the 2800–3000 cm^{-1} region as the electrolyte concentration increases up to 0.5M. The free OH band at 3749 cm^{-1} shows a slight decrease in intensity. The bands at 3660 and 3535 cm^{-1} show a constant behaviour with increasing electrolyte concentrations, indicating a constant energy of interaction with increasing electrolyte coverage. The persistence of the 3660 and 3535 cm^{-1} bands and the slight decrease in the free OH band show that the electrolyte adsorption occurs mainly on the free OH band. It seems that at low electrolyte concentrations (0.1–0.4M) competition between Cl^- and SD^- to be adsorbed on the hydroxyl groups of silica occurs until the threshold concentration (0.5M) at which the changes in SDS morphology and structure are attained and consequently a progressive increase in adsorption takes place.

Fig. 6 shows the SDS adsorption on the modified silica catalyst with varying electrolyte concentrations. By comparing the spectra of Figs. 5 and 6, it can be noted that an apparent decrease in intensity of the 3749 cm^{-1} band upon the addition of Mo is confirmed. H-bonded pairs of silanols of bands near 3720 cm^{-1} (free OH), 3535 cm^{-1} (OH...OH), and silanols, which are perturbed by interparticle contact of a band near 3660 cm^{-1} were detected.

The 3720 cm^{-1} band was largely eliminated with electrolyte concentrations up to 0.5M, leaving relatively perturbed bands at 3660 and 3500 cm^{-1} . Furthermore, the band height at 3749 cm^{-1} (isolated SiOH) is considerably diminished at the electrolyte concentration 0.5M compared with the corresponding spectra in Fig. 5. This indicates that

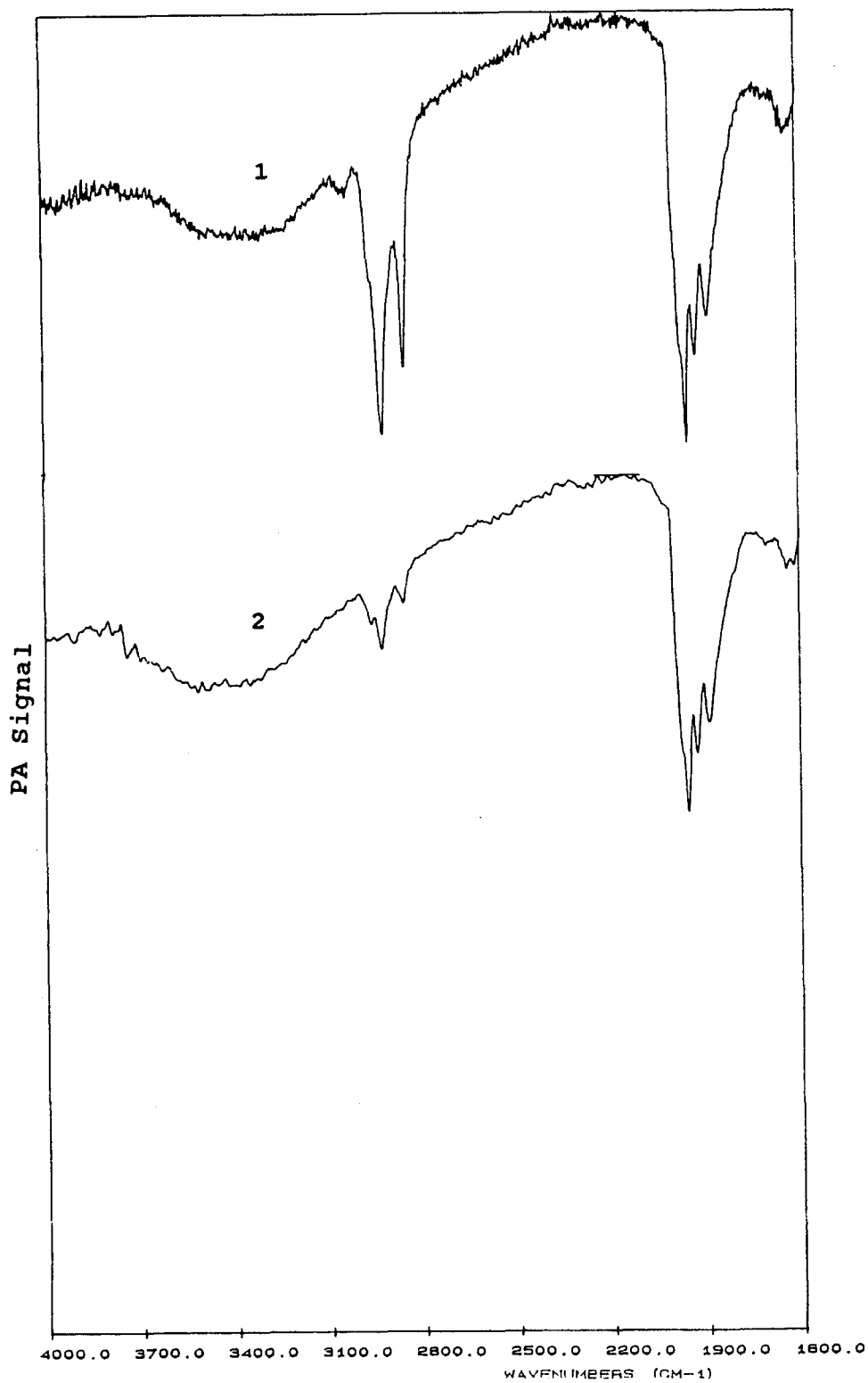


Fig. 3. FTIR-PA spectra of CTAB (1) and SDS (2) adsorbed onto ammonium heptamolybdate previously calcined at 773 K.

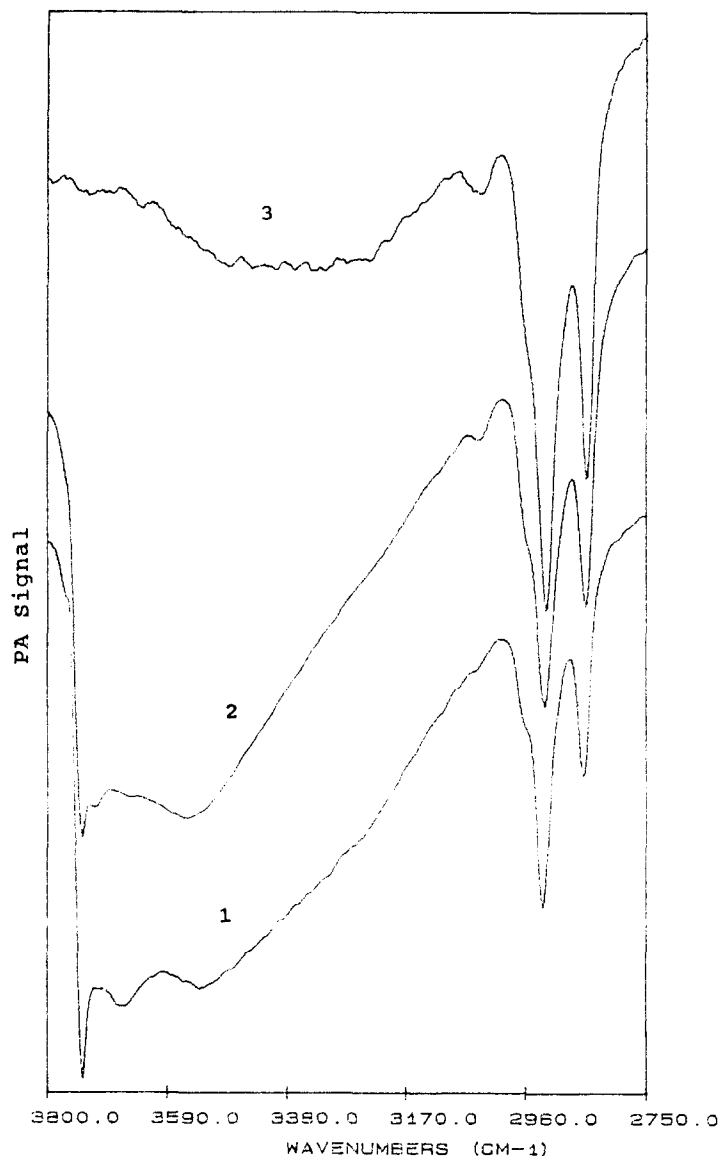


Fig. 4. High-frequency FTIR-PA spectra of CTAB adsorbed onto 1, silica-CTAB; 2, Mo-silica-CTAB; 3, Mo-CTAB.

the addition of Mo to silica definitely reduces the possibility of competition between Cl^- and SD^- to a much lower degree than in the case of Fig. 5; this is evidenced by the earlier enhancement of the C–H stretching region in the modified samples.

It has been found that H-bonded silanols are more reactive than isolated silanols for SDS adsorbed onto silica and Mo-modified silica catalysts, in the presence of an electrolyte. This was

confirmed by finding the ratio (R) of the peak height of the isolated (3749 cm^{-1}) silanols to that of the H-bonded (3500 cm^{-1}) silanols. Low values of R were obtained for both catalysts (3.8 for silica and 4.8 for Mo-silica) where a lower value of R was indicated for the silica catalyst, i.e. H-bonded silanols are relatively more reactive than isolated silanols. At high electrolyte concentrations (0.4–0.5M) we obtained excessive increases in the

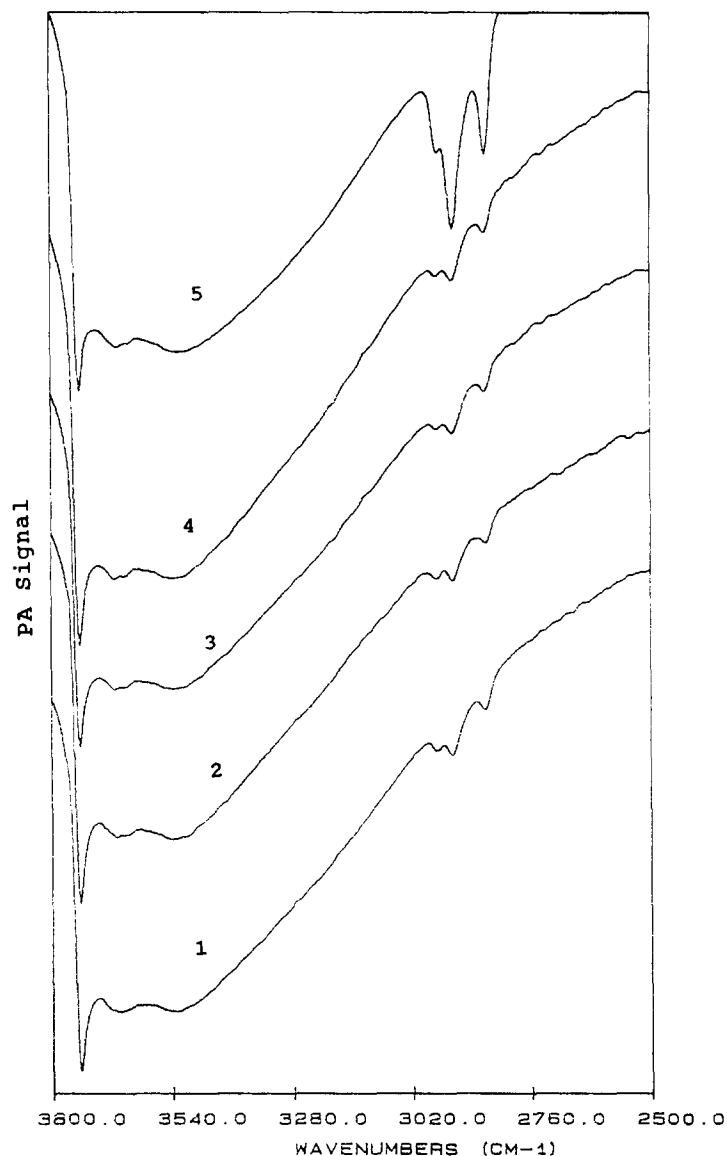


Fig. 5. High-frequency FTIR-PA spectra of SDS adsorbed onto silica as a function of the electrolyte concentration (NaCl): 1, 0.1M; 2, 0.2M; 3, 0.3M; 4, 0.4M; 5, 0.5M.

stretching frequencies of the SDS hydrocarbon chains. This reflects the dependence of the adsorption enhancement on the Mo oxide species, i.e. the presence of Mo on the silica surface promotes the formation of the flexible rod-like micelles of SDS earlier at low electrolyte concentrations compared with those of non-modified silica (Fig. 5) at similar electrolyte concentrations.

The adsorption of CTAB onto Mo-silica catalyst was also measured at different electrolyte concentrations. As an example, Fig. 7 shows the IR spectra recorded following CTAB adsorption onto Mo-silica at electrolyte concentrations of 0.5, 0.6 and 0.7M. The surfactant adsorption led to a decrease in the free OH band at 3749 cm^{-1} (at 0.5M NaCl) which was slightly intense than the

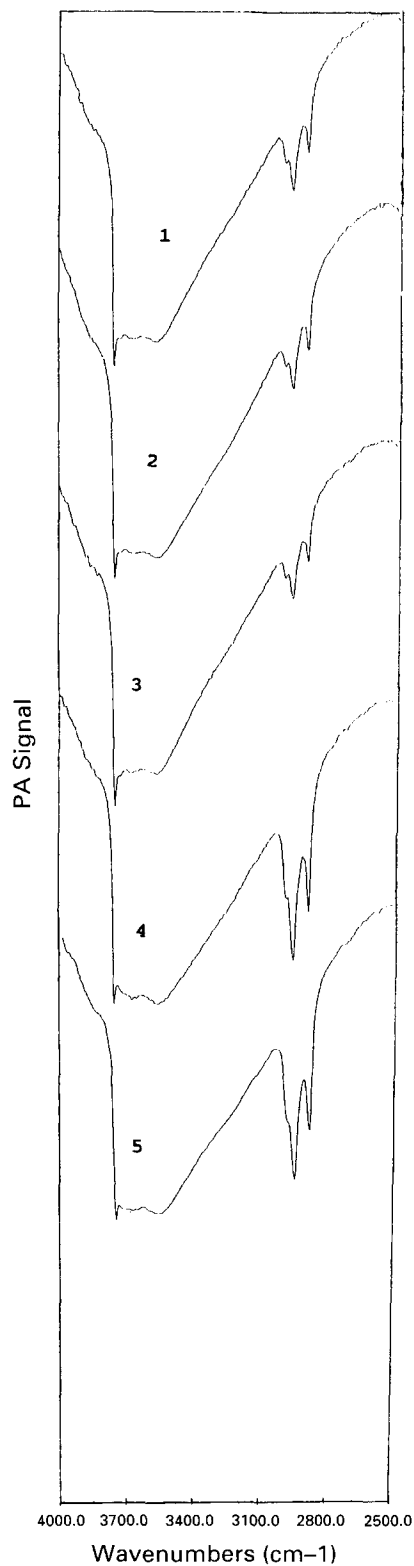


Fig. 6. High-frequency FTIR-PA spectra of SDS adsorbed onto Mo-silica catalyst as a function of the electrolyte concentration (NaCl): 1, 0.1M; 2, 0.2M; 3, 0.3M; 4, 0.4M; 5, 0.5M.

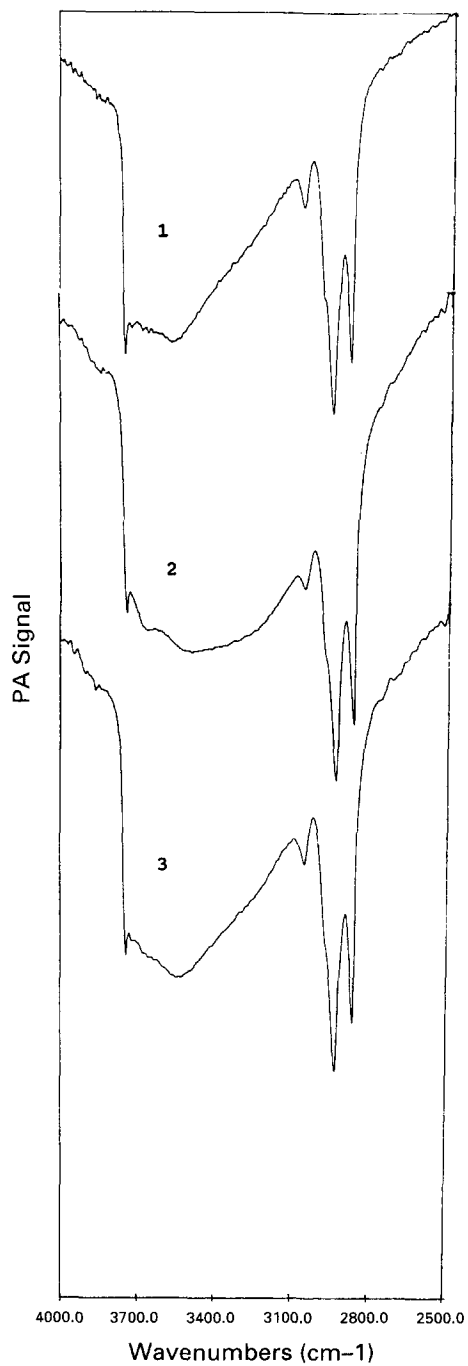


Fig. 7. High-frequency FTIR-PA spectra of CTAB adsorbed onto Mo-silica catalyst as a function of the electrolyte concentration (NaCl): 1, 0.5M; 2, 0.6M; 3, 0.7M.

corresponding spectrum obtained at the same electrolyte concentration for SDS surfactant (Fig. 6). This indicates that SDS participates more with the free hydroxyl groups than CTAB. This possibility was confirmed by the existence of all types of hydrogen bonding in CTAB surfactant (Fig. 7).

Upon increasing the electrolyte concentration (0.6 and 0.7M) we observed a further decrease in the free OH band and the ultimate disappearance of the 3720 cm^{-1} band. The perturbed bands at 3660 and 3500 cm^{-1} were formed at an electrolyte concentration of 0.6M. However, the 3660 cm^{-1} band ultimately disappeared at an electrolyte concentration of 0.7M, whereas the corresponding increase in intensity of the 3500 cm^{-1} band was retained. This means that the trapped water (3660 cm^{-1}) gradually decreases, enhancing the amount of bound water at 3500 cm^{-1} upon increasing the electrolyte concentration. This behaviour was more obvious with CTAB surfactant than with SDS, emphasizing the idea that CTAB is involved with H-bonding silanols.

Furthermore, the condensed charged CTAB micelle, which has a longer alkyl chain than SDS, of a thick phase should be directed towards the H-bonding silanols because of steric influences that could exist upon the adsorption on the free hydroxyl groups [23]. Of particular interest is the IR feature at 3041 cm^{-1} , which shows the dependence on the presence of Mo, as shown in Fig. 4, and the chemical identity of the anion in the solid [24].

No significant change in this band was found throughout the spectra in Fig. 7. This means that Cl^- ions have no effect on either the frequency or the intensity. The enhancement of this band upon increasing the Mo content [25] confirms that the head group of the surfactant could be oriented to the accessible MoO_3 species created on the silica surface.

4. Conclusions

The effect of added NaCl and Mo in enhancing the adsorption of ionic surfactants onto silica has been confirmed using the FTIR-PA technique in

the solid state, as well as adsorption isotherms from solution. This suggests that the changes in the surfactant structure, confirmed by the isotherms, are also reflected from IR, in which a formal change should have occurred parallel to that observed in solution.

Upon adsorption onto silica and Mo-silica catalysts, both CTAB and SDS showed significant alterations in the hydroxyl group region. The number of accessible sites on the silica surface for H-bonding interactions increases as the apparent chain length of the reacting micelle increases (e.g. CTAB). However, restricted interactions for the short alkyl chains were found only on the free hydroxyl groups (e.g. SDS).

References

- [1] C. Gamboa and L. Sepulveda, *J. Colloid Interface Sci.*, 113 (1986) 566.
- [2] H.A. Scherage and J.K. Backus, *J. Am. Chem. Soc.*, 73 (1951) 5108.
- [3] P. Lianos and R.J. Zana, *J. Phys. Chem.*, 84 (1980) 3339.
- [4] D. Bendedouch and S.H. Chen, *J. Phys. Chem.*, 88 (1984) 648.
- [5] T. Imae, R. Kamiya and S. Ikeda, *J. Colloid Interface Sci.*, 108 (1985) 215.
- [6] M.A. Yoskie and J.H. Harwell, *J. Phys. Chem.*, 92 (1988) 2346.
- [7] M.M. Mohamed and E.F. Vansant, *Thermochim. Acta*, 217 (1993) 91.
- [8] B.H. Bijsterbosch, *J. Colloid Interface Sci.*, 47 (1974) 186.
- [9] M. Lindheimer, E. Keh, S. Zaini and S. Partyka, *J. Colloid Interface Sci.*, 138 (1990) 83.
- [10] L. Ter-Minassian-Saraga, *J. Chem. Phys.*, 63 (1966) 1270.
- [11] Y. Gushikem and M.S. Iamamoto, *J. Colloid Interface Sci.*, 134 (1990) 275.
- [12] J.C. Moreira and Y. Gushikem, *Anal. Chim. Acta*, 176 (1985) 263.
- [13] J.H. Fendler and W.J. Fendler, *Catalysis in micellar and Macromolecular System*, Academic Press, New York, 1975.
- [14] M.J. Rosen, *Surfactant and Interfacial Phenomena*, Wiley, New York, 1987.
- [15] H. Ruppercht, *Kolloid-Z. Z. Polym.*, 249 (1971) 1127.
- [16] T. Barr, J. Oliver and W.V. Stubbings, *J. Soc. Chem. Ind.*, 67 (1948) 45.
- [17] M.M. Mohamed and E.F. Vansant, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 96 (1995) 253.
- [18] M.M. Mohamed, *Spectrochim. Acta A*, 51 (1995) 1.
- [19] M.M. Mohamed and G.M. El-Shafi, *Spectrochim. Acta A*, 51 (1995) 1525.

- [20] G.M. El-Shafi and M.M. Mohamed, *Colloids Surfaces A: Physicochem. Eng. Aspects*, 94 (1995) 267.
- [21] C.A. Bunton, K. Ohmenzette and L. Sepulveda, *J. Phys. Chem.*, 81 (1977) 2000.
- [22] B.A. Morrow and A.J. McFarlan, *J. Non-Cryst. Solids*, 120 (1990) 61.
- [23] T. Imae, A. Abe and S. Ikeda, *J. Phys. Chem.*, 92 (1988) 1548.
- [24] K. Winnett, *Appl. Spectrosc.*, 44 (1990) 687.
- [25] M.M. Mohamed, PhD Thesis, Al-Azhar University, Egypt (1991).