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Application of calorimetric methods to the adsorption of surfactants from solution [1]

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Abstract

The adsorption and desorption behaviour of non-ionic (Triton X-305) and anionic (cetylpyridinium chloride) surfactants at various oxides (alumina, silica gel, titania, tin dioxide) have been investigated by means of several calorimetric methods (immersion calorimetry, solution calorimetry, liquid-flow adsorption calorimetry). It is shown that the application of different calorimetric methods, which are sensitive to various partial processes of adsorption, is able to provide new insights into the mechanism and thermodynamics of such a complex process as surfactant adsorption onto solid surfaces.

INTRODUCTION

The adsorption and desorption of surfactants at solid surfaces is of great scientific as well as technological interest. In particular, the modification of surface properties by surfactant adsorption is an essential step in many technological processes. However, scientific understanding of this phenomenon is limited because of the complex character of this process which is influenced by a large number of parameters. Therefore, there is a great demand for the development and application of various experimental methods sensitive to different changes in properties during the adsorption process, for example, changes in structure (spectroscopic methods) or energy (calorimetric methods) [1].

During the last decade, remarkable progress has been made in the application of adsorption calorimetry as an independent experimental method to the study of adsorption processes and to the elucidation of the mechanism of surfactant adsorption [2–12].

The adsorption of surfactants is characterized by a complex superposition of various partial reactions including: interaction of the solvent with the surface of the adsorbent; interaction of the surfactant with the surface

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and/or the double layer; solvent–surfactant interaction; surfactant–surfactant interaction, etc. These are all accompanied by appropriate heat effects: enthalpy of immersion of the adsorbent in the pure solvent; enthalpy of displacement and enthalpy of adsorption; enthalpy of dilution; enthalpy of micellization and enthalpy of surfactant aggregation in the adsorption layer (hemi-micellization).

Calorimetry is a method that provides integral data summarized over all processes occurring in the reaction cell of the apparatus. The correct interpretation of calorimetric results obtained from a complex adsorption experiment requires, therefore, additional information on the enthalpy contribution of the different steps mentioned above.

Therefore, three different calorimetric techniques (immersion calorimetry, solution calorimetry and liquid-flow adsorption calorimetry) were applied to the study of surfactant adsorption in our laboratories. It is the aim of this contribution to describe the calorimetric procedures and to demonstrate the efficiency of these methods by reporting some typical results on the adsorption and desorption of non-ionic (Triton X-305) and cationic (cetylpyridinium chloride) surfactants onto different oxides (silica gel, alumina, TiO_2 and SnO_2) under various conditions (pH, electrolyte concentration, temperature).

EXPERIMENTAL

Materials

The non-ionic alkylphenylpolyglycolether C_8H_{17}–C_6H_4(–OCH_2–CH_2–$)_{30}$-OH (Triton X-305) was supplied by Merck, Germany, and used as delivered. It was a high purity sample with less than 0.5% impurities (mainly water) and polydisperse in the ethoxy chain length. The critical micelle concentration (cmc) determined by surface tension measurements was 1 mmol l^{-1} at 25°C.

Cetylpyridinium chloride monohydrate (CPCl) was also obtained from Merck and recrystallized twice from an acetone/ethanol mixture. Its cmc at 25°C was estimated to be 0.85 mmol l^{-1}, in good agreement with the literature value of 0.9 mmol l^{-1} at 20°C [13].

Some important properties of the oxides are shown in Table 1. All the absorbents used were p.a. grade samples, washed several times with bidistilled water and dried at 150°C. A particle size fraction of 50–90 μm was separated for use with the flow methods to guarantee a low, reproducible flow resistance of the solid in the adsorption cells. The pH at zero point of charge (pzc) was determined by streaming-potential measurements using a PCD 02 (Muetek GmbH, Germany), at different pH levels and interpolating to zero potential.

TABLE 1

Properties of the adsorbents used

Adsorbent	Specific surface area (BET) in $m^2 g^{-1}$	pH at pzc
α-Alumina (ALCOA, USA)	4.0 ∓ 0.1	8.7 ∓ 0.2
Silica gel A (Kieselgel 60, Merck, Germany)	212 ∓ 5	2.2 ∓ 0.1
Silica gel B (Fractosil 1000, Merck, Germany)	21.1 ∓ 0.4	2.0 ∓ 0.1
TiO_2 rutile (Bayer AG, Germany)	6.7 ∓ 0.2	6.1 ∓ 0.1
SnO_2 (Laborchemie Apolda, Germany)	6.3 ∓ 0.2	4.2 ∓ 0.2

Immersion calorimetry

The immersion experiments were carried out by means of a precision reaction calorimeter LKB 8700 (LKB Produkter AB, Sweden) equipped with a 25 cm^3 reaction cell and a special-purpose glass ampoule ($V_{max} = 1.5\ cm^3$) with a capillary tip (Fig. 1). The solid adsorbent was loaded into the ampoule and pretreated at 150°C in a vacuum (10^{-2} Pa) to obtain a reproducible clean surface. After being sealed, the part of the amoule containing the sample was introduced into the reaction cell that contained 25 cm^3 of pure water. After thermal equilibrium was reached, immersion was started by depressing the ampoule holder (stirrer) and breaking the capillary. The measured heat effect had to be corrected for the heat of breaking the tip and for evaporation effects. This was done by measuring the blank effects for the "dead-space" of the ampoule [14, 15]. The uncertainty of the heat measurement was less than 10 mJ.

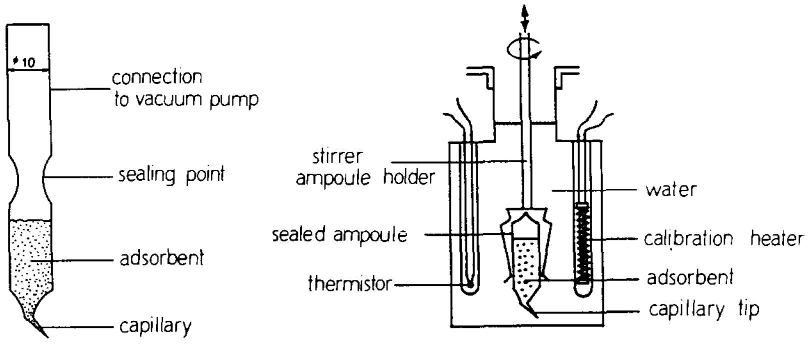

Fig. 1. Calorimetric cell and ampoule for immersion calorimetry.

Solution calorimetry

Measurements of solution and dilution enthalpies were performed with the same calorimeter as described above, using a standard glass ampoule ($V = 1\ \mathrm{cm}^3$) and a reaction cell with a sapphire breaking pin in its base. The measuring uncertainty was similar to that in the immersion experiments.

Flow adsorption calorimetry

A scheme of the highly sensitive flow adsorption calorimeter is shown in Fig. 2. It is a Calvet-type microcalorimeter equipped with a flow system consisting of several heat exchangers and a special adsorption cell. The calorimeter is characterized by a minimal detectable heat effect of 1 μW and a good long-term stability of the baseline. Further details concerning construction, properties and efficiency of the calorimeter as well as the measuring procedure were published in ref. 10. All adsorption and desorption measurements were carried out at a constant flow rate of $20\ \mathrm{cm}^3\ \mathrm{h}^{-1}$, using, as a rule, a cumulative procedure for quantiative measurements, i.e. the concentration of the surfactant solutions was increased or decreased stepwise after reaching the appropriate equilibrium state. This was necessary to minimize dilution effects which are difficult to correct in flow calorimetry. In addition, the surfactant solutions had to be degassed carefully (vacuum degassing) to avoid the sampling of air bubbles in the adsorption cell, especially at higher temperatures.

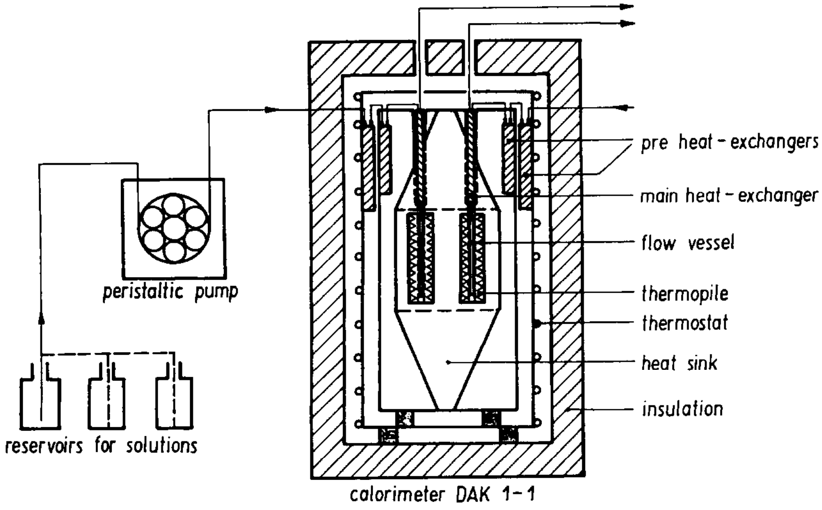

Fig. 2. Scheme of the liquid-flow adsorption microcalorimeter.

Adsorption isotherms

The adsorption isotherms corresponding to the calorimetric results were also measured by means of a flow method working under the same experimental conditions as in the flow calorimeter and using UV or IR detectors for recording the surfactant concentration at the outlet of the adsorption column. The amount of surfactant adsorbed was calculated from the retention volumes [6, 16, 17]. The adsorption isotherms of CPCl on silica gel at different temperatures were determined by a static method. The suspensions (50 cm^3 surfactant solution +0.5 g silica gel) had been stirred for 3 h at the desired temperature and the equilibrium concentration of CPCl in the supernatant was analysed by UV spectrometry.

RESULTS AND DISCUSSION

Immersion experiments

Immersion calorimetry may be regarded as a method of monitoring the interaction of solid surfaces with liquids, such as water in this case. This interaction is sensitive to small changes in the surface state parameters (chemical nature, crystallinity, microprosity, surface area), provided that the sample preparation and the experiment is properly done [18].

In a previous paper [19], we reported results for different types of synthetic silicas. It could be shown that there are typical values of the specific enthalpy of immersion which depend on the conditions of the synthesis.

The results for the oxides used in this work are summarized in Table 2. The specific enthalpies of immersion for these oxides are very different. However, plotting the data against the pH at pzc (Fig. 3) provides a nearly linear relation. This basic relationship between the enthalpy of immersion and the acidity of the surface hydroxyl groups has already been derived quantitatively by Healy and Fuerstenau [20]. It is only valid for insoluble inorganic oxides in the absence of microporosity.

TABLE 2

Specific enthalpies of immersion of the adsorbents in water at 25°C

Adsorbents	Specific enthalpy of immersion in mJ m^{-2}
α-Alumina	-633 ∓ 20
Silica gel A	-274 ∓ 5
Silica gel B	-218 ∓ 5
TiO_2	-520 ∓ 15
SnO_2	-412 ∓ 16

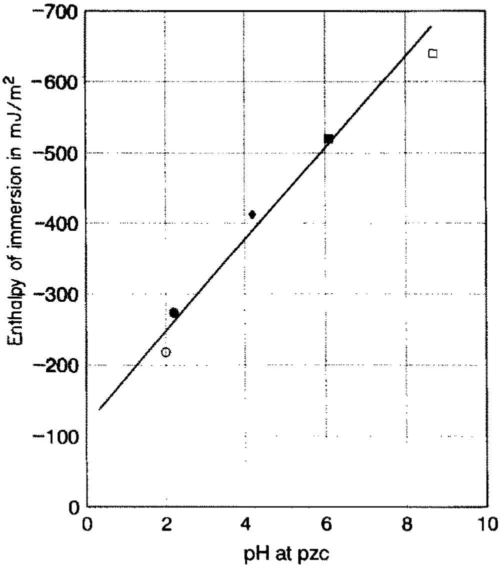

Fig. 3. Plot of the specific enthalpies of immersion of the adsorbents in water against the pH at pzc. ●, silica gel A; ○, silica gel B; □, alumina, ■, titania; ◆, tin dioxide.

Solution calorimetry

A knowledge of the solution and dilution enthalpies in surfactant solutions is required for the correction of dilution effects as well as for the estimation of aggregation effects in solution as also in the adsorption layer (enthalpy of micellization or hemi-micellization). Figure 4 shows the enthalpies of dilution per mole of Triton X-305 of a concentrated stock solution ($C_0 = 0.2\,\mathrm{mol/l^{-1}}$) plotted against the final concentration. The dilution process of this non-ionic surfactant is exothermic. Therefore, the micellization is endothermic and an enthalpy of micellization of 10 kJ $\mathrm{mol^{-1}}$ has been evaluated at 25°C.

Calorimetric results for the enthalpies of solution per mole of CPCl for different concentrations and temperatures are shown in Fig. 5. For CPCl, the enthalpies of solution are endothermic and the enthalpies of micellization are exothermic in the temperature range investigated. However, the micellization process seems to be strongly temperature-dependent (Table 3). Furthermore, the enthalpy of micellization should change from exothermic to endothermic below 20°C. Similar behaviour of other alkylpyridinium chlorides has been reported by Mehrian et al. [21].

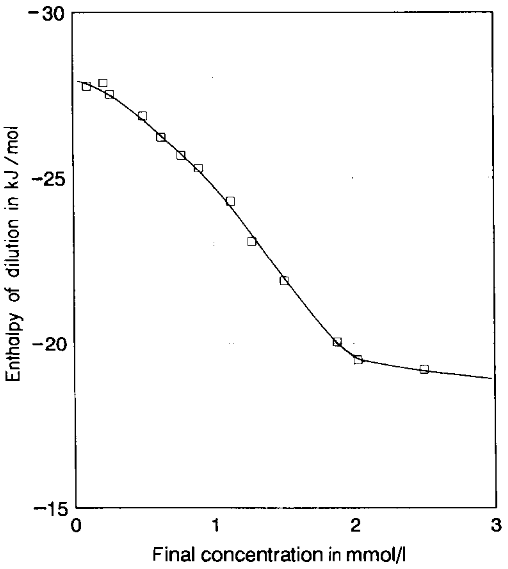

Fig. 4. Enthalpy of dilution of Triton X-305 vs. the final concentration (intial concentration, 0.2 mol l^{-1}) at 25°C.

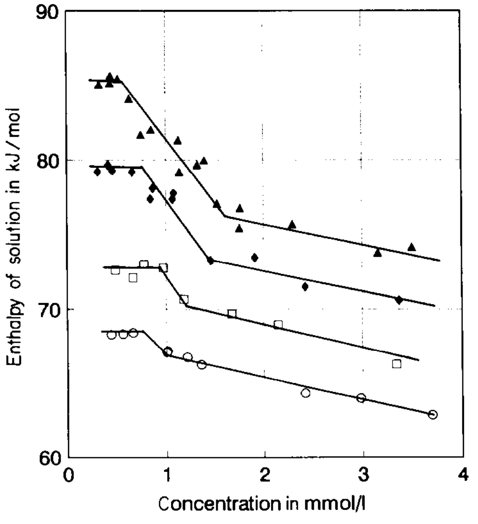

Fig. 5. Enthalpies of solution of CPCl in water at various temperatures: ○, 25°C; □, 30°C; ■, 35°C; ▲, 40°C.

TABLE 3

Enthalpies of micellization of CPCl at different temperatures

Temperature in °C	Enthalpy of micellization in kJ mol^{-1}
25	-1.6 ∓ 0.2
30	-3.0 ∓ 0.2
35	-5.8 ∓ 0.3
40	-9.4 ∓ 0.3

Flow adsorption calorimetry

The liquid-flow technique provides information on the interactions taking place in the adsorption layer (surfactant–solid surface or double layer, surfactant aggregation, displacement of solvent). The measured heat corrected by dilution effects is usually called the enthalpy of displacement [3, 18]. The flow technique is less universal than the batch methods (ampoules, titration), because fine powders cannot be used, but it has notable advantages. It enables the study of desorption phenomena and is an effective method for screening the influence of different parameters such as pH, electrolyte concentration, etc. Experimentally determined adsorption and enthalpy isotherms of Triton X-305 onto different oxides are shown in Figs. 6 and 7. It was found that the adsorption behaviour strongly depends on the surface properties of the adsorbents. Adsorption onto TiO_2 and SnO_2 is very weak, whereas the adsorption onto silica gel is an order of magnitude higher. The heat effects are generally small, only a few mJ m^{-2}; for TiO_2, no heat effect could be detected. At alumina and SnO_2, only endothermic enthalpies of displacement were measured in the concentration range investigated. A different result was obtained for the adsorption onto silica gel. There are obviously two opposite processes taking place: an exothermic process at low concentrations and an endothermic process at higher concentrations. A plot of the differential molar enthalpies of displacement against the surface coverage is more convenient for interpretation, as shown in Fig. 8. The results are similar to batch titration calorimetric data reported by Lindheimer et al. [22]. Based on the calorimetric results and on the fluorescence spectroscopic results of Levitz et al. [23], the adsorption behaviour of Triton X-305 onto oxides can be described as follows. At low concentrations, single molecules attach to the surface by hydrogen bonds, this is expressed by exothermic heat effects. This process is obviously strong for silica gel, but is weak for the other oxides investigated so that it could not be detected. At higher surfactant concentrations, the adsorbed surfactant molecules form aggregates resulting in endothermic differential molar enthalpies of displacement comparable with the appropriate enthalpies of micellization in solution.

The calorimetric recordings shown in Fig. 9 illustrate the overlapping of

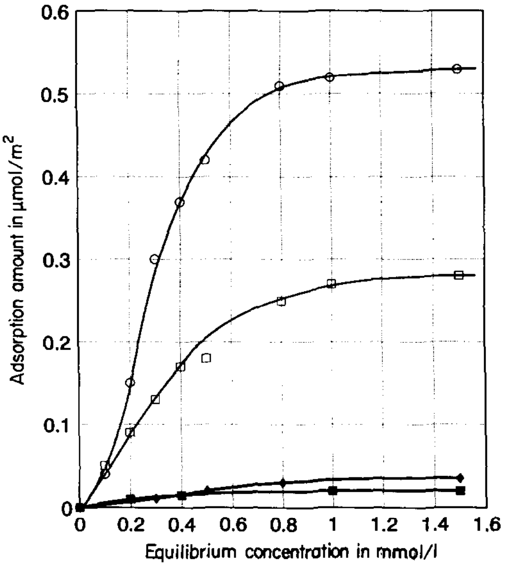

Fig. 6. Adsorption isotherms of Triton X-305 at different oxides, $T = 25°C$: ○, silica gel A; □, alumina; ■, titania; ◆, tin dioxide.

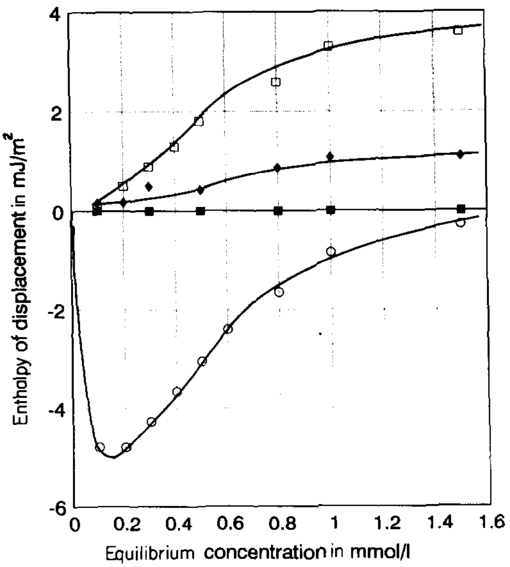

Fig. 7. Enthalpies of displacement of Triton X-305 vs. equilibrium concentration at different oxides, $T = 25°C$: ○, silica gel A; □, alumina; ■, titania; ◆, tin dioxide.

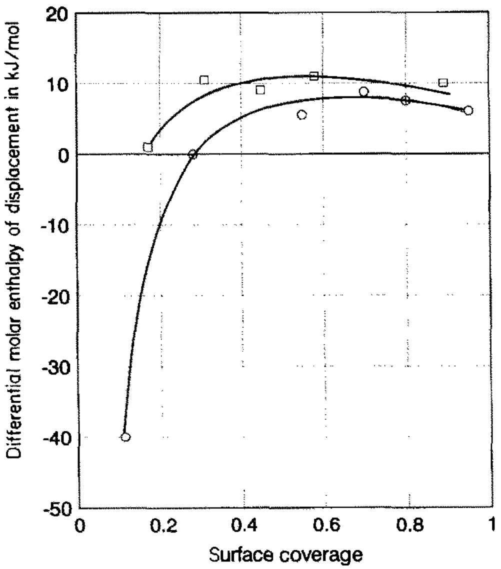

Fig. 8. Differential molar enthalpies of displacement of Triton X-305 vs. surface coverage at 25°C: ○, silica gel A; □, alumina.

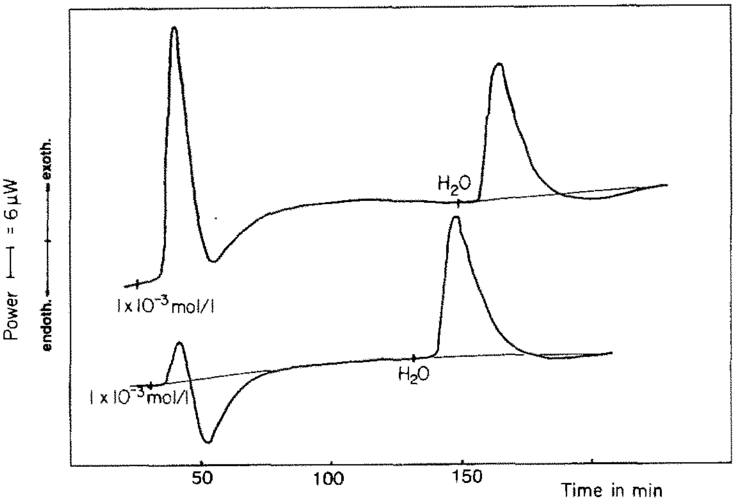

Fig. 9. Calorimetric recordings of two successive adsorption–desorption runs of Triton X-305 at silica gel A, $T = 25°C$.

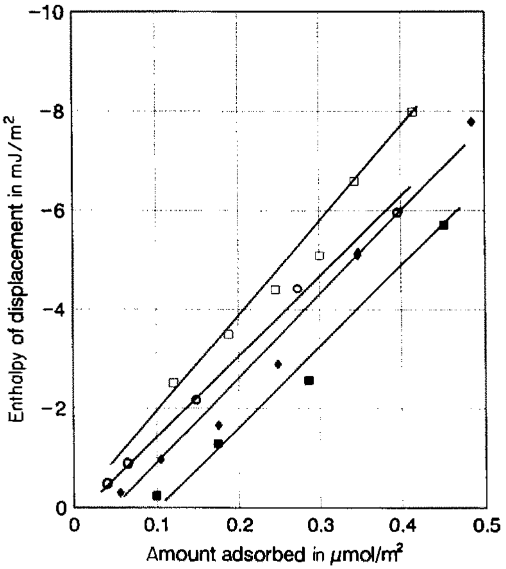

Fig. 10. Plot of the enthalpies of displacement against amount of CPCl adsorbed at 25°C, pH, 5.6: ○, silica gel A; □, alumina; ■, titania; ◆, tin dioxide.

the two adsorption stages. The two stages also show different desorption behaviours. The two successive adsorption–desorption runs with the same sample (desorption time approx. 3 h) were performed. The results suggested that the surfactant aggregates are desorbed completely over a short period (similar exothermic peaks), whereas the directly bonded surfactant molecules desorb slowly and possibly incompletely (the exothermic adsorption effect in the second run is much lower).

In a recently published paper [11], we reported results for the adsorption of CPCl onto the same oxides. Some selected calorimetric results are shown in Figs. 10–12. The enthalpies of displacement are exothermic over the whole concentration range investigated. The plot of the enthalpies of displacement against the amount of CPCl adsorbed are straight lines with approximately the same slope (which represents the differential molar enthalpy of displacement) for all oxides, although the surface charges of the oxides are different. This suggests uniform adsorption mechanism. Furthermore, it is obvious that the adsorption is strongly influenced by the electrolyte content as well as by the pH of the surfactant solution, as expected for an electrostatic mechanism coupled with hemi-micellization. Refering to Fig. 10, the aggregation of the surfactant molecules seems to contribute only a little to the heat effects measured. This is supported by the relatively small enthalpy of micellization of CPCl at 25°C (see Table 3).

Owing to the large temperature dependence of the micellization process, measurements at higher temperatures were performed with silica gel as adsorbent (Figs. 13 and 14). In accordance with the exothermic enthalpies

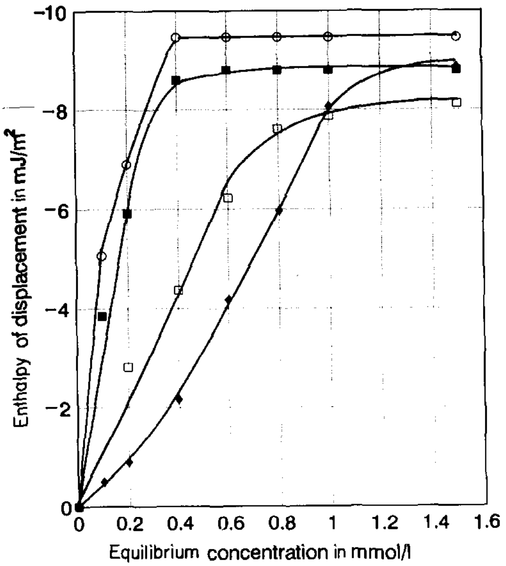

Fig. 11. Effect of KCl concentration on the enthalpies of displacement of CPCl at silica gel A, $T = 25°C$, pH 5.6: ◆, pure water; □, 1 mmol l^{-1} KCl; ■, 5 mmol l^{-1} KCl; ○, 10 mmol l^{-1} KCl.

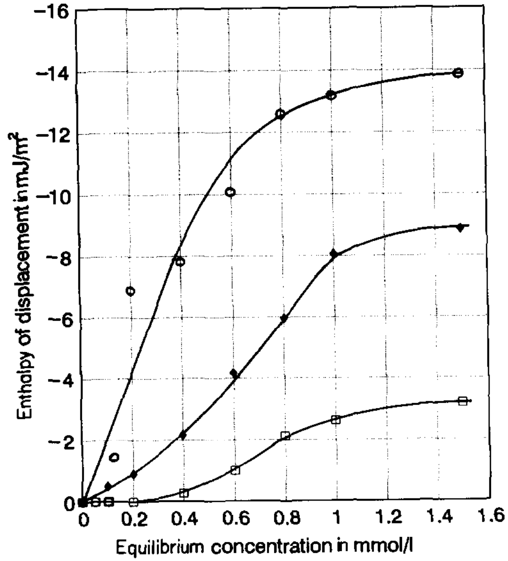

Fig. 12. Effect of pH on the enthalpies of displacement of CPCl at silica gel A, $T = 25°C$: ◆, pH 5.6; □, pH 4.0; ○, pH 9.5.

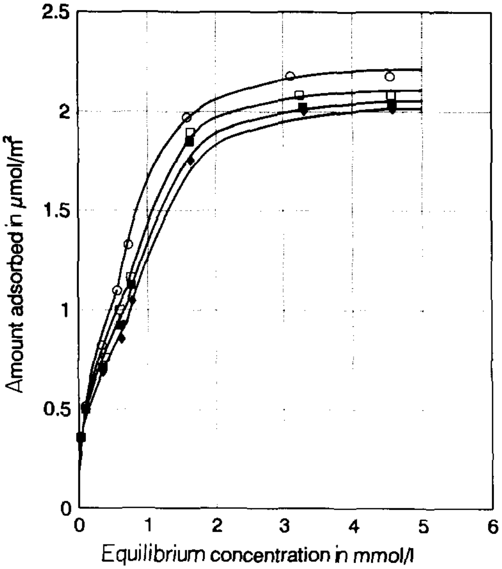

Fig. 13. Adsorption isotherms of CPCl at silica gel B at various temperatures, pH 5.6: ○, 25°C; □, 30°C; ■, 35°C; ◆, 40°C.

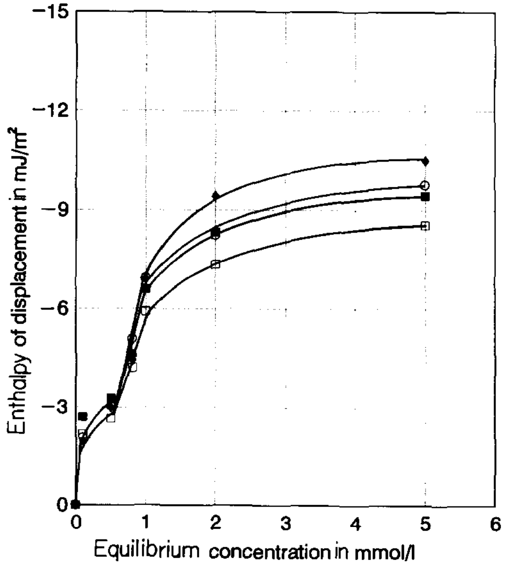

Fig. 14. Enthalpies of displacement of CPCl at silica gel B at various temperatures, pH 5.6: ○, 25°C; □, 30°C; ■, 35°C; ◆, 40°C.

of displacement, the amount adsorbed decreases with increasing temperature. However, an analysis of the enthalpy data shows that the step in the enthalpy isotherms in the vicinity of the cmc, which is caused by surfactant aggregation, increases at temperatures above 30°C. This can be explained by the increasing exothermic enthalpy contribution of the hemimicellization in the region of the cmc (overcompensation of the decreasing number of adsorbed molecules).

In future, more work will be done to assess the important influence of temperature on adsorption, especially in a more quantatitive manner.

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