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Thermochimica Acta 310 (1998) 199–205

thermochimica acta

Thermochemical investigations of coordinatoclathrates with fluorenyl groups[1]

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Received 16 May 1997; received in revised form 27 June 1997; accepted 30 June 1997

Abstract

The interactions of clathrate-forming host compounds with different solvent vapours in a concentration range up to 1500 ppm were investigated with a thermal sensor. The used thermopile chip gave the possibility to record small amounts of heat power with short response times. The correlation between the signal parameters (area, height) and concentration of vapour is linear. The differences between the sensitivities of the different host–guest combinations are significant. The determination of the amount of guest molecules, included by the host compounds, as a function of the partial pressure leads to the result that clathrate formation only takes place near saturation pressure. The same perception was applied for measurements of the heat of sorption as a function of the weight of the layer on the thermopile chip. The reaction seems to be controlled by a surface process. © 1998 Elsevier Science B.V.

Keywords: Clathrates; Inclusion; Solvent vapor; Thermal sensor

1. Introduction

During the last decade supramolecular chemistry has occupied an important place in biological and chemical research and, increasingly, also in commercial applications because of its ability to control and design the specific intermolecular interactions.

A new class of supramolecular compounds are the clathrates [1]. Clathrates are multimolecular crystalline inclusion compounds, where the so-called guest molecules are included in holes of the crystalline lattice of a host compound. The investigated host compounds belong to the group of coordinatoclathrates [2]. The formation of these clathrates is controlled by steric factors and specific electronic interactions and proceeds from co-crystallization as well as from solid–gas reaction with solvent vapours. These properties suggest the use of such substances for applications as sensor coating materials for the analytical detection of solvent vapours.

In particular the influence of the steric factor opens new possibilities for increasing the selectivity of the inclusion reaction. For the identification of clathrates, normally X-ray, NMR and TG–DSC methods are applied [3–6].

The primary results concerning the use of these compounds as coatings for sensors with gravimetric and dielectric transducers are available [7,8].

It is proposed to use a thermal transducer for the detection of solvent vapours, as long as every reaction

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[1] Presented at the Twelfth Ulm-Freiberg Conference, Freiberg, Germany, 19–21 March 1997

PII S0040-6031(97)00397-3

is accompanied by a heat effect. Hence, the existing differences in the enthalpies give an additional independent information and increase the selectivity [9]. This requires estimation of the applicability of the hosts in a thermal sensor for solvent vapours. The important factors for the characterization of the sensor reaction are: the equilibrium behaviour, the reproducibility of the signals and the sensitivities. The properties of thermal sensors are mainly influenced by the heat power, which results from the rate and the enthalpy of the sensor reaction. All these parameters are determined thermodynamically and kinetically and their corresponding data have to be registered.

2. Experimental

Fig. 1 shows the formula of the investigated host compounds. In principle, they consist of a bulky fluorenyl-skeleton and may have bulky substituents attached to 2,7-position, hydroxyl and spacer units.

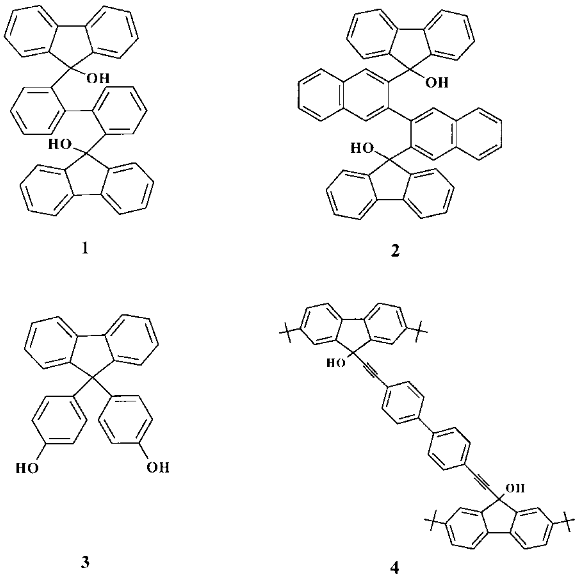

Fig. 1. Formula of the host compounds: 1=2,2′-*bis*(9-hydroxy-9-fluorenyl)biphenyl; 2=3,3′-*bis*(9-hydroxy-9-fluorenyl)-2,2′-binaphtyl; 3=4,4′-(fluorenyl-9,9-diyl)-diphenol; and 4=9,9′-(biphenyl-4,4′-diyl-diethynyl)-*bis*(2,7-t-butylfluoren-9-ol).

The main part of the experimental work was carried out by means of a special flow-through chip calorimeter that is designed in the same manner like a thermal sensor (Fig. 2). The heat-power transducer for the detection of the heat-flow changes is a silicon-chip with monolithic integrated silicon thermopiles [10]. The layers of the crystalline host compounds were prepared by gently dropping the solutions of the host on the active site of the thermopile chip followed by evaporation and drying. The gas flow is modulated

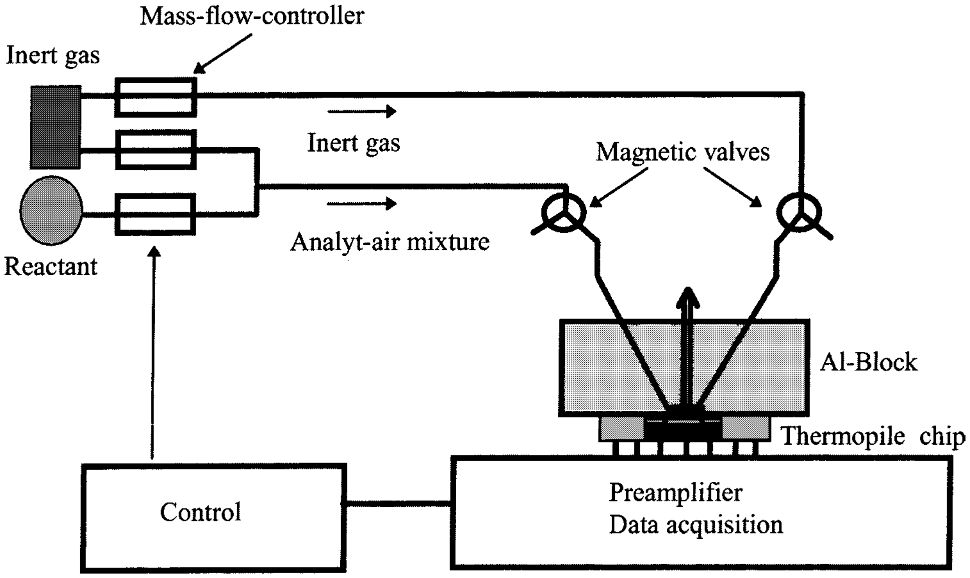

Fig. 2. Gas flow set-up.

by periodically switching between the channels of the inert gas and that of the mixture of organic vapour with synthetic air by means of magnetic valves. Both channels lead directly into the etched cave of the silicon chip. Because of the small size of the cave (20 μl) the mixing time constant is very low. This results in fast and rectangular-shaped partial pressure variations near the host layer and hence to high heat-power values. Periodical pulses could be generated as a result of the reversible process of the reactions. The generated heat-power signals are accumulated and then recorded to increase the signal-to-noise ratio. The separately measured zero-effect values are eliminated from the curves. The gas dosing of this experiment is prepared in special bags which contain a mixture of gas and air under a predetermined concentration level. The variation of the gas concentration could be controlled by means of the mass-flow controllers. A significant advantage of the described equipment is the high dynamical sensitivity of the thermopile chip. According to the low time constant of the thermopile chip and also to the fast concentration change, small heat pulses could be detected, recorded and kinetically evaluated without high expense of deconvolution. Fig. 3 shows a typical accumulated and corrected curve resulting from a partial-pressure change impulse of acetone and Host 1.

3. Results and discussion

Using the described equipment, interactions between the host compounds and solvent vapours in a concentration range up to 1500 ppm were investi-

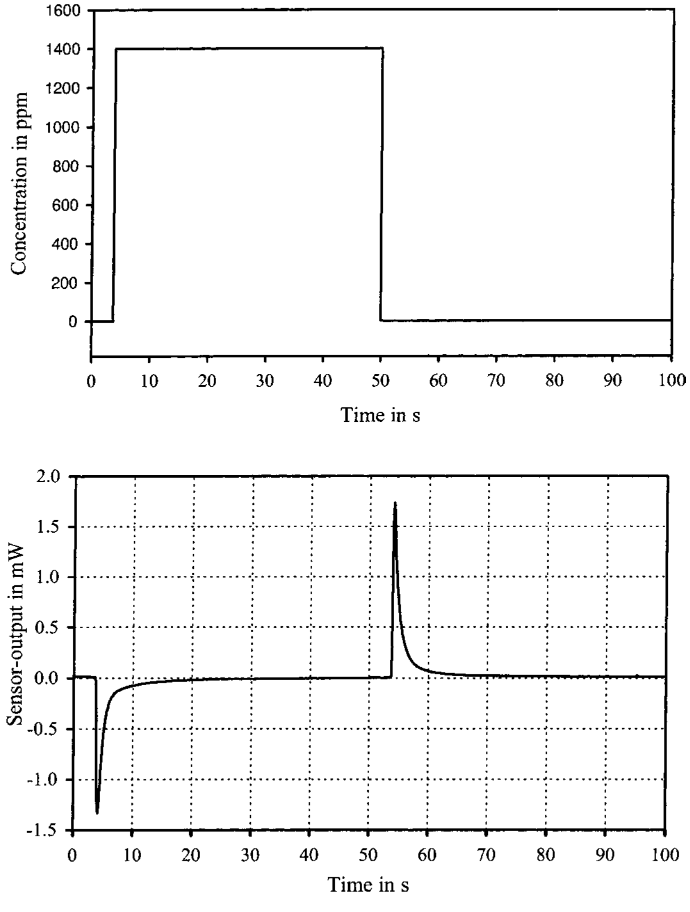

Fig. 3. Sorption and desorption of acetone with Host 1 (concentration of vapour: 1400 ppm).

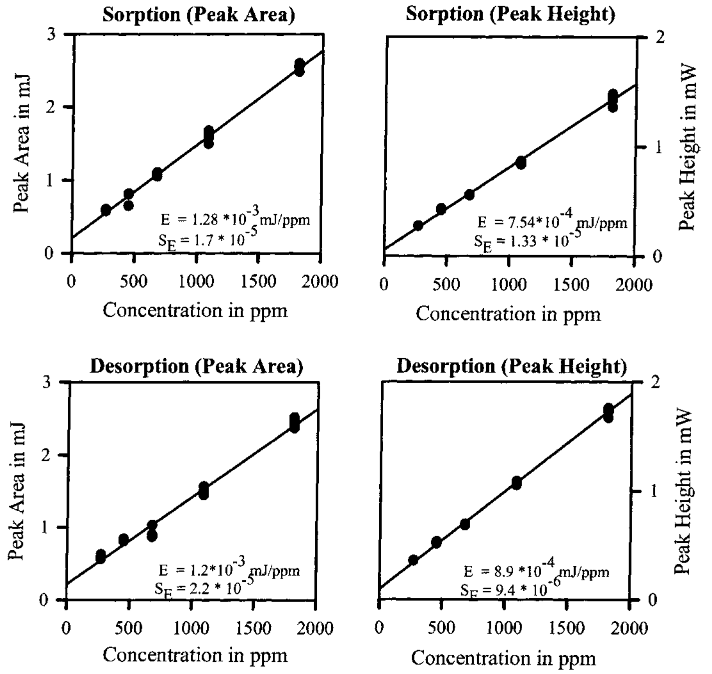

Fig. 4. Dependence of the signal parameters (area, height) from the concentration of vapour: Host 1-acetone; e=sensitivity; and s_e=standard deviation.

gated. An important parameter for the sensor and at the same time for the determination of the thermodynamical equilibrium behaviour is the dependence between the signal values and the concentration of the analyte gas (Fig. 4). This connection is investigated for a number of host–guest combinations. In the used concentration range, the signal parameter is linearly correlated with the partial pressure of the analyte gas. The slope is interpreted as analytical sensitivity. Since the reproducibility of the sensitivities lies in a small percentage range, significant differences in the sensitivities between the various host–guest pairs could be

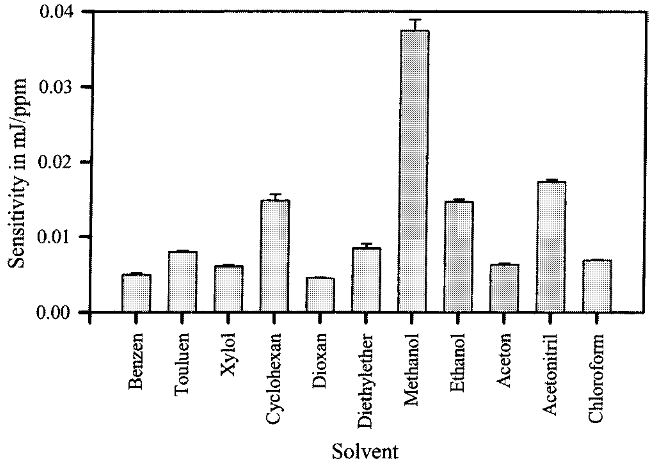

Fig. 5. Sensitivity of the area of sorption of Host 4 against different solvents.

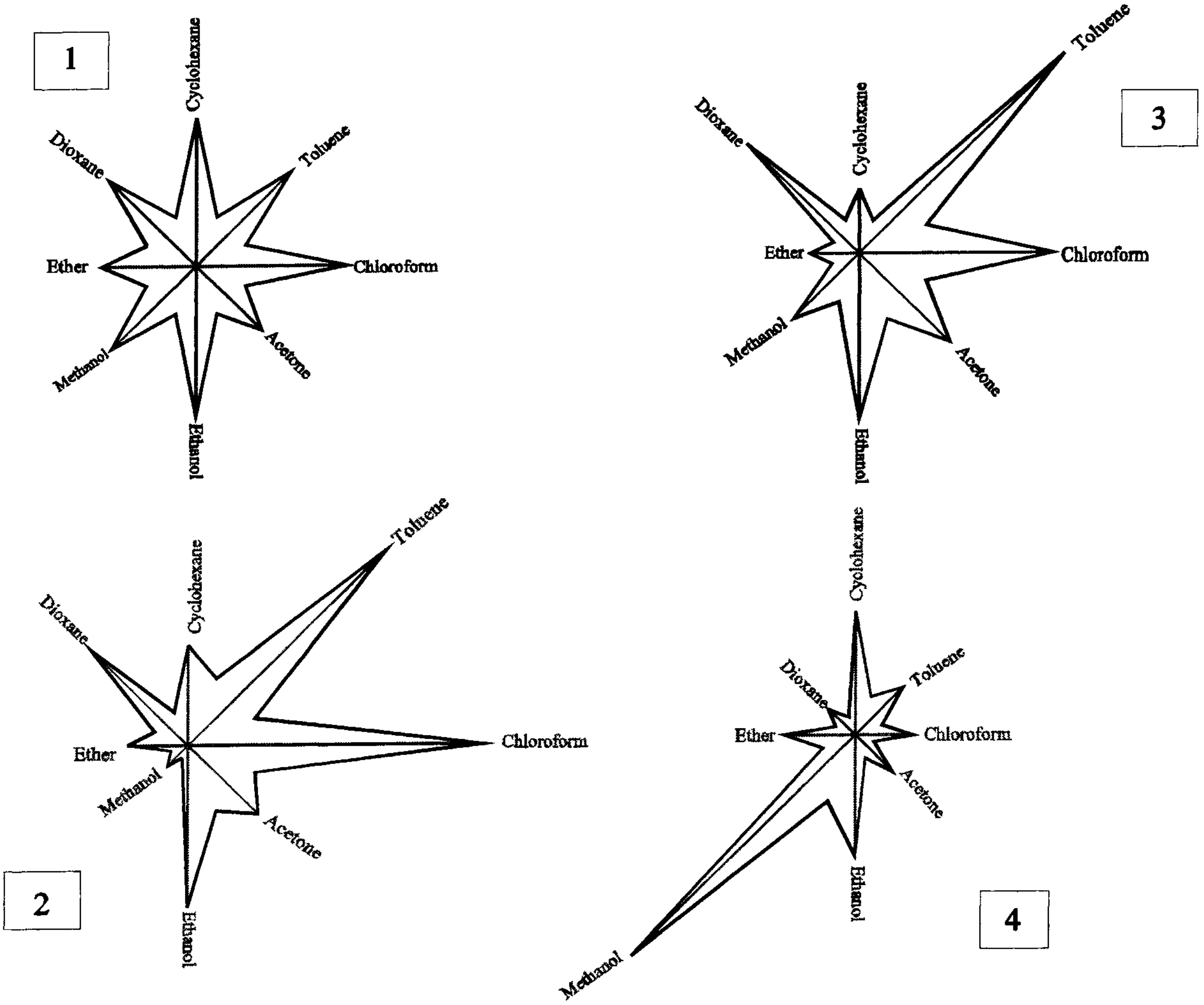

Fig. 6. Sensitivities of hosts 1,2,3,4 against different solvents (lengths of the lines~sensitivity peak area sorption).

registered reliably. For the following considerations only the sensitivities of the sorption area are chosen because they show the lowest deviation.

Fig. 5 depicts the sensitivity of Host 4 according to different solvents. A remarkably high sensitivity could be seen in the case of methanol and Host 4. The sensitivities of all investigated host–guest systems are represented in Fig. 6. Hosts 2 and 3 show a similar behaviour, especially the conspicuous high sensitivity against toluene. Host 1 shows only small differences in the sensitivities, while the behaviour of Host 4 is completely different.

The aforementioned results rise the question of the reasons of the significant differences in the sensitivities. The considered area of the sorption peak represents the heat of sorption that is determined by the enthalpy and the amount of guest included. The amount included in dependence of the partial pressure of the solvent vapour is measured by means of a micro balance. Fig. 7 shows such a curve for the Host 1 – methanol system over the whole concentration range until saturation point. From the above findings, we come to the conclusion that, only near the saturation pressure, the included guest amount abruptly rises till

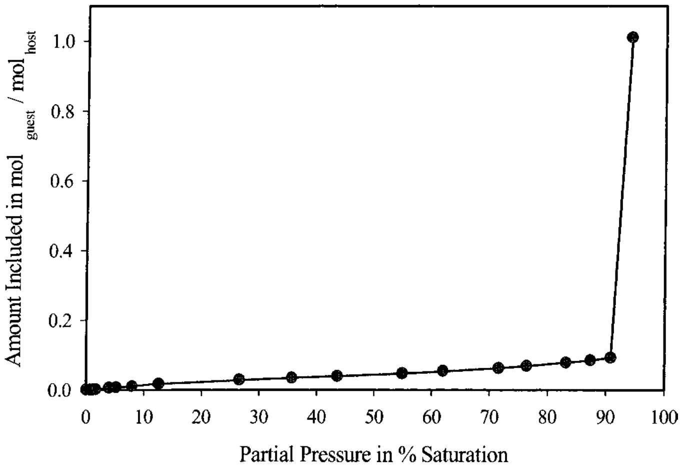

Fig. 7. Dependence of amount guest included from partial pressure of vapour host 1 – methanole.

a defined stoichiometry of 1 : 1 is reached. Therefore it is assumed that below this range no clathrate formation occurs, while only a surface adsorption or diffusion process occurs. To obtain an exact quantity for the amount included in the concentration range up to 1500 ppm was difficult, because the experimental conditions of the balance and the calorimeter are different.

Another evidence for the incomplete clathrate formation in this concentration range was detected by measuring the heat of sorption as a function of the mass of the layer on the thermopile chip (Fig. 8 and 9). The correlation between the considered peak area of sorption and the weight of the layer is not linear. That means that the interaction between host and guest could not catch the bulk coating. On comparing all hosts it is seen that this behaviour is different. The results of X-ray diffraction and TG–DSC measurements give the conclusion that the lattice is rebuilt in a very slow process in order to form a clathrate. Compared with the short response times of the calorimetric sensor (100–150 s), it probably seems that the heat-producing reaction on the thermopile chip is controlled by a surface process.

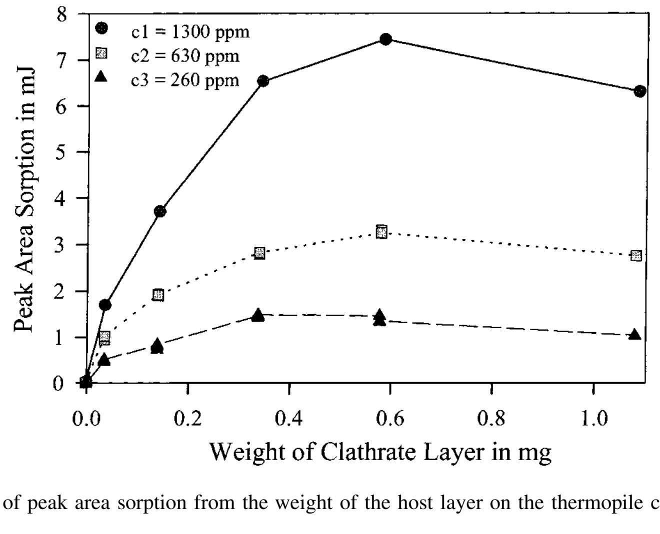

Fig. 8. Dependence of peak area sorption from the weight of the host layer on the thermopile chip Host 1– acetone.

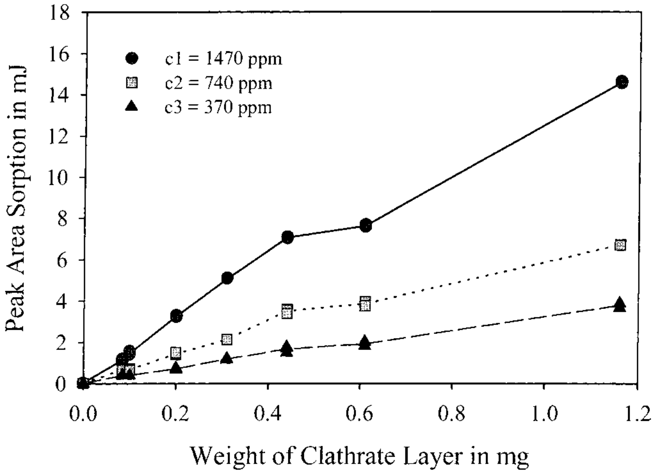

Fig. 9. Dependence of peak area sorption from the weight of the host layer on the thermopile chip Host 4 – benzene.

More information is expected by the calculation of time constants and the finding of a kinetic model for the reaction followed by an explanation of the mechanism of the reaction.

4. Conclusion

The interactions between host and guest are reliable and measurable in the described calorimeter but the signals are caused not only by a clathrate formation. The acquisition of small heat-power pulses is possible because of the high dynamical sensitivity of the thermopile chip. Because of the significant differences in the sensitivities between the different host–guest systems the compounds are interesting for sensor applications.

To use the clathrate formation in a range of low solvent-vapour concentration as sensor reaction hosts with permanent pore lattice is necessary.

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