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Thermochimica Acta 271 (1996) 141–148

thermochimica
acta

Thermochemical study of clathrate-forming host-guest reactions for the detection of organic solvent vapours[1]

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Received 1 June 1995; revised version received 9 June 1995; accepted 9 June 1995

Abstract

The clathrate formation of a crystalline host with acetone and methanol vapours has been studied by means of simultaneous TG-DSC measurements in isothermal and scanning mode of operation. The directly measured enthalpies of inclusion at 25°C for acetone (–47.8 kJ mol^{-1}) and methanol (–48.6 kJ mol^{-1}) are significantly higher than known thermal desorption enthalpy data from DSC measurements. Concentration dependent measurements indicate a nearly linear concentration dependence for both the amount of guest included and the heat effect over a wide range supporting the recently suggested importance of this class of supramolecular hosts as chemical sensitive coating materials for sensor applications. Inclusion experiments at different temperatures indicate a strongly decreasing inclusion ability with increasing temperature.

Keywords: Inclusion compound; Clathrate; Solvent vapour; TG-DSC; Enthalpy of inclusion

1. Introduction

During the last decade supramolecular chemistry has occupied an important place in chemical and biological research and increasingly also in commercial applications because of its ability to control and design the specific intermolecular interactions. However, only the exact knowledge of the energetic and steric properties of the interactions allows the synthesis and optimization of novel structures with tailor-made properties [1].

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[1] Presented at the 11th Ulm Conference, Freiberg, Germany, 29–31 March, 1995.

SSDI 0040-6031 (95) 02561-8

Recently, host compounds capable of forming multimolecular crystalline inclusions (clathrates) with a variety of organic guest molecules have been reported [2–5]. The formation of these clathrates is controlled both by steric factors and more specific interactions between host and guest, e.g. hydrogen bonds [3–5], which opens new possibilities for increasing the selectivity of the inclusion reaction. Although clathrate formation is carried normally out by co-crystallization from solution, the enclathration may also proceed by a heterogeneous solid-gas reaction and this promises sensor uses [2]. First results on the use of these host compounds as chemical-sensitive coatings for sensor applications have already been published [6,7].

Whereas the structure and the formation properties of these clathrates involving a variety of different organic guest molecules are reasonably known, less reliable information on thermodynamic data and on the mechanism of the enclathration are available. This prompted the present study. Here we report on first calorimetric and microgravimetric results of the clathrate formation of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl host compound (Fig. 1) with acetone and methanol vapour in dependence of temperature and concentration. Special attention is directed to the evaluation of reliable interaction enthalpies and to the inclusion stoichiometry which are important for analytical sensor applications and for the discussion of the nature of the existing phase equilibria.

2. Experimental

The host compound 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (Fig. 1) was obtained in the highest available purity (>99%) from the Institute of Organic Chemistry in Freiberg. The synthesis and structural details are described in Refs. [2,8].

The organic guest compounds acetone and methanol were p.a. grade chemicals from Merck, Germany.

Calorimetric and microgravimetric measurements were carried out by means of the simultaneous TG-DSC 111 from Setaram, France. The gas delivery system of the device was modified for measurements under well-defined concentrations of the organic vapours in air. Concentrations below saturation were prepared by evaporation of weighed amounts of solvent in a definite volume of air using polypropylene sample bags (Tedlar

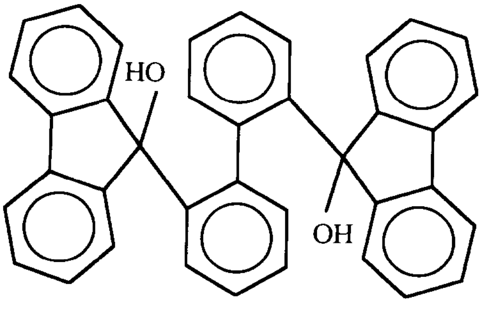

Fig. 1. Formula of the model host compound.

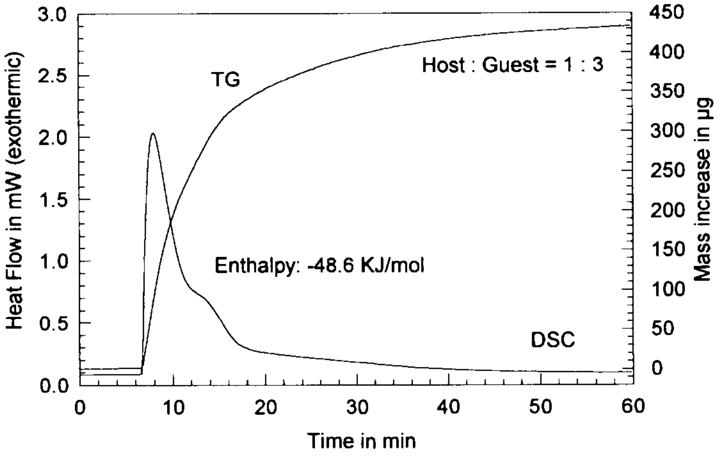

Fig. 2. Experimental TG-DSC curves for methanol inclusion at 25°C and saturation concentration (23°C) in air (sample weight 2.41 mg).

Sample Bags, SKC Inc., USA). The concentrations were checked by gas chromatography. Saturated gas mixtures were prepared using a temperature controlled saturator filled with the pure solvent. Pure or solvent loaded air was pumped continuously through the system at a flow rate of 30 ml min^{-1} by means of a peristaltic pump.

The pure host compound was weighed (2–4 mg) into the sample pan (open aluminium pan) and an adequate amount of alumina was filled into the symmetric reference pan of the TG-DSC device. Due to the symmetric design of both the microbalance and the calorimeter, blank effects (buoyancy changes, differences in heat conduction) were very

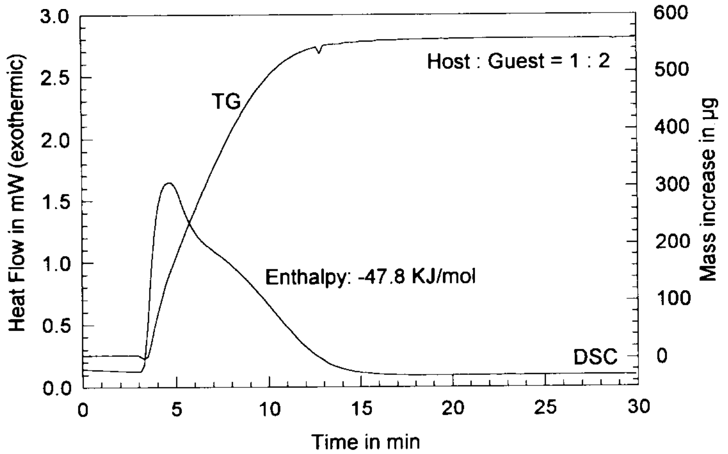

Fig. 3. Experimental TG-DSC curves for acetone inclusion at 25°C and saturation concentration (23°C) in air (sample weight 2.57 mg).

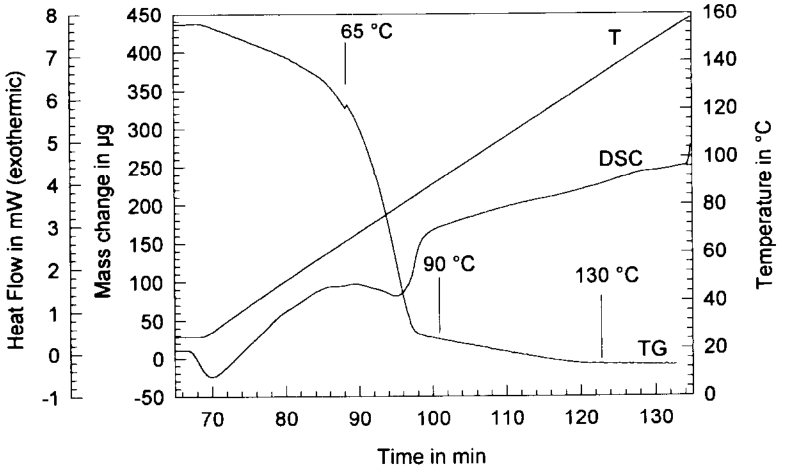

Fig. 4. Results of thermal degradation of the methanol clathrate by temperature scanning at 2 K min^{-1} and constant composition of the gas atmosphere (same sample as in Fig. 2).

small and easy to correct or neglected, especially at lower concentrations. Generally, the inclusion experiments were performed in the isothermal mode of operation to achieve the highest possible accuracy. Only for the study of the thermal stability of the clathrates, temperature scanning at 2 K min^{-1} was applied at constant composition of the gas phase.

The experimental uncertainties of the calorimetric and microgravimetric results were determined to be ±5 mJ and ±3 µg, respectively.

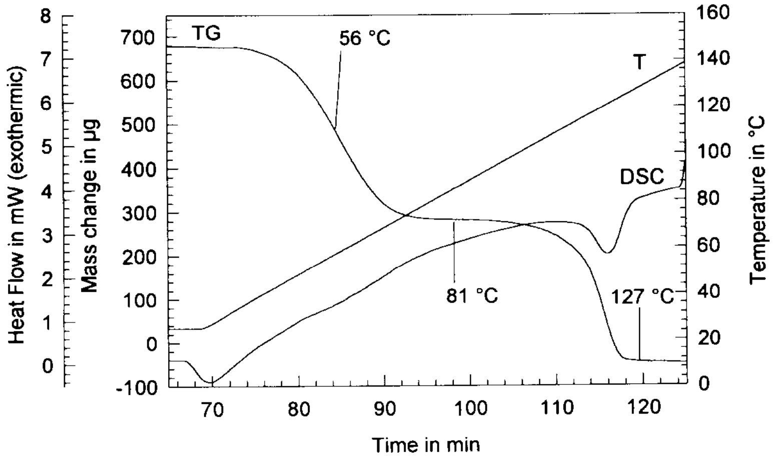

Fig. 5. Results of thermal degradation of the acetone chlathrate by temperature scanning at 2 K min^{-1} and constant composition of the gas atmosphere (sample weight: 3.00 mg).

3. Results and discussion

The TG-DSC 111 is especially well suited for the investigation of solid-gas equilibria because of its ability to determine both the amount of the gaseous component included and the corresponding heat effect simultaneously. The results for methanol and acetone isothermal inclusions (25°C) at saturation concentration in air are shown in Figs. 2 and 3, respectively. The curves indicate that the inclusion process could be divided into different steps. A fast first stage of inclusion with high power output is followed by one (acetone) or two (methanol) slower stages accompanied by appropriately lower heat effects. This finding is in agreement with quartz microbalance measurements [7] and tests with a calorimetric sensor [9]. The stoichiometric composition of the clathrates formed at equilibrium corresponds to the stoichiometry of the clathrates, which results from co-crystallization from solution [2]. The measured enthalpies of inclusion of –48.6 ± 0.8 kJ mol^{-1} for methanol and –47.8 ± 0.7 kJ mol^{-1} for acetone are significantly higher than thermal desorption enthalpy data reported in the literature; e.g. –10 kJ mol^{-1} for the acetone clathrate [6,7], indicating that obviously not only weak interactions occur.

The results of thermal desorption measurements using the temperature scanning mode are presented in Figs. 4 and 5. The thermal degradation of the clathrates is also characterized by multiple stages. The acetone clathrate is disassembled in two clearly separated steps with nearly the same height. This behaviour corresponds to X-ray structure data

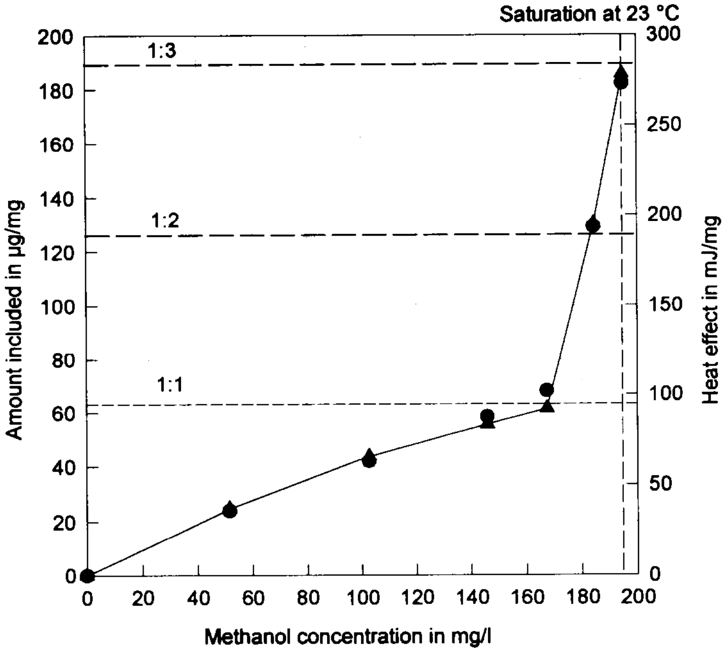

Fig. 6. Plots of the amount of methanol included (●) and the heat effect (▲) against the concentration in the gas phase at 25°C.

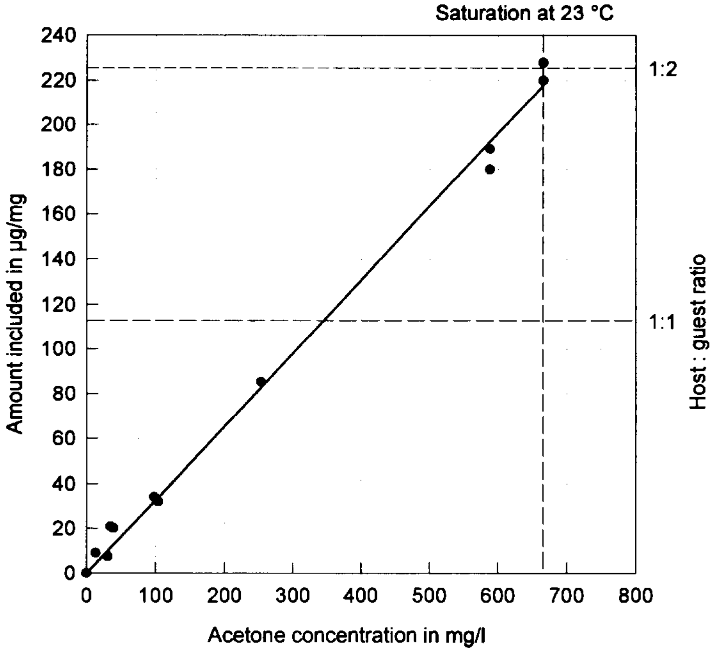

Fig. 7. Plot of the amount of acetone included against the concentration in the gas phase at 30°C.

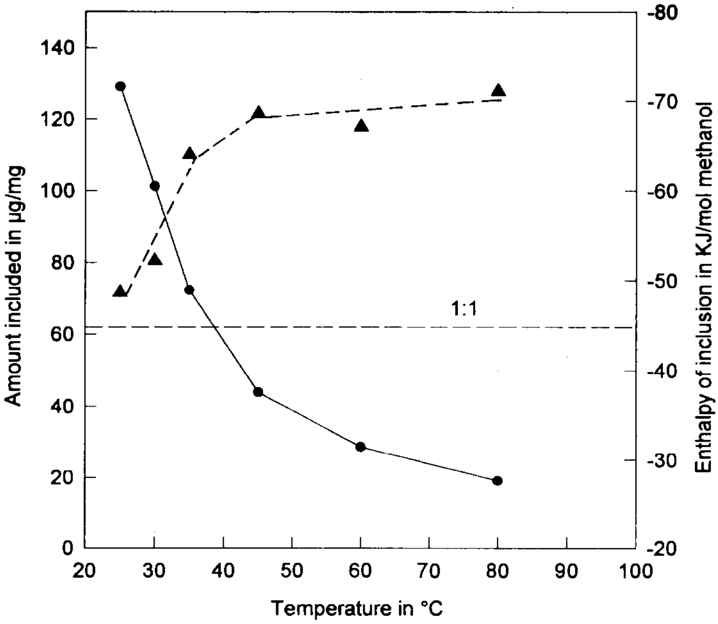

Fig. 8. Temperature dependence of the amount of methanol included (●——●) and the molar enthalpy of inclusion (▲– – –▲) at constant composition of the gas phase (saturation at 23°C).

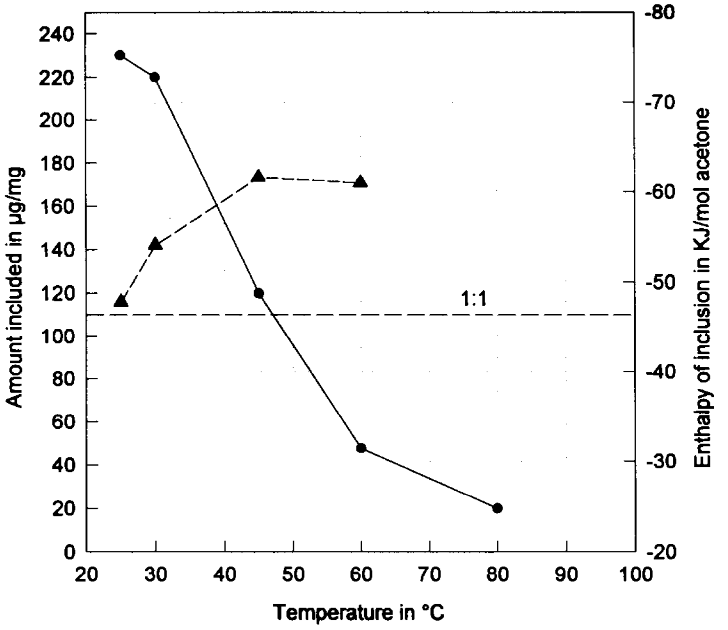

Fig. 9. Temperature dependence of the amount of acetone included (●——●) and the molar enthalpy of inclusion (▲– – –▲) at constant composition of the gas phase (saturation at 23°C).

reported in [3] that distinguish between two differently bonded guest molecules. One molecule is hydrogen bonded to the host while the other occupies a cavity between fluorenyl groups on two adjacent hosts. The situation with the methanol clathrate seems to be more complicated. Although three steps of degradation can be observed as expected from the stoichiometry and the inclusion experiment, an assignment of the stages is difficult because of the poor correlation of the heights with stoichiometry and the flowing transitions between the steps.

The concentration and temperature dependencies of the amount of vapours included are of great importance for the discussion of the possible mechanism and phase equilibria or sensor application. For instance, the existence of definite stoichiometric compounds should cause sharp stages while a sorption mechanism leads to a steady increase of the amount included with concentration. The experimentally determined concentration dependencies are illustrated in Figs. 6 and 7 showing a nearly linear relationship between amounts of guest included and concentration over a wide range. Only for methanol inclusion is there a steep increase of inclusion near saturation concentration from a host to guest ratio of 1:1–1:3. It is also remarkable that the heat effects show a similar concentration dependency resulting in a uniform molar enthalpy of inclusion of –48 kJ mol^{-1} over the concentration range investigated.

The temperature dependence of the inclusion process is described in Figs. 8 and 9. It is evident that the amount of vapour included is strongly decreasing with temperature. In contrast with the included amounts, the molar enthalpies of inclusion become more exothermic up to a temperature of 45°C and remaining nearly constant above this temperature. The beginning of the plateau apparently correlates with the decrease of the host to guest ratio below 1:1 indicating a change in the inclusion mechanism. However, an analogous behaviour could not be detected in the isothermal experiments where equal molar enthalpies of inclusion were found below and above a host to guest ratio of 1:1.

4. Conclusions and summary

Simultaneous TG-DSC measurements have been successfully applied to the study of the enclathration process of organic solvent vapours into the solid host compound 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl. Both the TG and heat flow signals indicate that the inclusion process consists of two or more reaction steps distinguished by the reaction rate. The directly measured molar enthalpies of inclusion are very similar for methanol and acetone (-48 kJ mol^{-1}) but significantly higher than recently published values of thermal desorption enthalpies. The composition of the clathrates at 25°C is similar to that obtained by co-crystallization from solution. The investigation of the inclusion in dependence on the concentration of the guest in the gas phase indicates an approximately linear relationship for both the amount included and the heat effect over a wide range of concentration. The study of the temperature influence shows that the enclathration is strongly temperature dependent expressed by a fast decrease of the amount of guest included with temperature. These results suggest a sorption like mechanism rather than a stoichiometric reaction but for a clear decision further systematic physico-chemical investigations are necessary including additional experimental methods (equilibrium pressure measurements, X-ray diffraction, precision microcalorimetry) and simulation calculations. Moreover, the results demonstrate the high potency of this type of supramolecular host compounds as chemical-sensitive coating materials for both mass and thermal sensitive devices in sensor applications.

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