

Application for Extension of Financial Support of

**Project 2:
Transient and Equilibrium Measurement
of Sorption on Zeolites**

as part of a package of proposals
aspiring joint support by CNRS, DFG, EPSRC and NSF

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1. General Information

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1.2. Topic

Transient and Equilibrium Measurement of Sorption of Gases on Zeolites

1.3. Code Word

Transient and Equilibrium Sorption

1.4. Research Areas

Material Sciences
Chemical Engineering
Physical Chemistry
Interface Sciences

1.5. Scheduled Total Duration of Support

six years, support by DFG since 2003

1.6. Period of Support Applied for

three years

1.7. Total Period of Support

support started November 2003,
extension requested starting from November 2006

1.8. Summary

This project is primarily dedicated to the measurement of the time dependence of gas adsorption on zeolite materials following a change of pressure in the surrounding atmosphere. Experiments are performed gravimetrically, i. e. by using a highly sensitive magnetic suspension balance (Rubotherm, Bochum). During the first period, the gravimetric device has been accomplished in such a way that two-component diffusion measurement have as well become possible. The influence of intracrystalline diffusion for the mass exchange process between the gas and the solid sorbent phase is investigated by varying size, amount and bed arrangements of the zeolite crystals and also by changing pressure steps in lengths and directions (i. e. performing ad- and desorption processes). Also the mode of activation of the sorbent material, its pre-treatment or history and the number of pressure cycles to which it had been exposed will be taken into account.

The project will deliver to the consortium the phenomenological uptake data as transport diffusivities obtained under transient conditions. Also gas adsorption equilibria, i. e. the adsorption isotherms (or adsorption isobars) will be determined. This information is necessary to calculate the thermodynamic factor correlating transport and self-diffusivities.

2. State of the Art, Own Activities in the Field

2.1. State of the Art

Studying molecular sorption under transient external conditions is among the first methods [1-3], and still today [4-6] the most common way, of measuring zeolitic diffusion. In the ideal case of total absence of external transport resistances (like the so-called bed [5, 7] and valve [5, 8-10] effects) the classical uptake and release experiments offer the most convenient boundary conditions in comparison with all other microscopic techniques.

As the main result of the work within the first period of the application, molecular transport in zeolites has been found to be subject to a hierarchy of transport resistances. As a consequence, for different observation ranges different types of resistances, including genuine intracrystalline diffusion, intracrystalline barriers and surface barriers, may become dominant. As one of the central challenges for the second period of applications it has to be demonstrated that these various transport limitations are in a consistent way revealed by the different measuring techniques. Molecular uptake and release may be affected by both intracrystalline and extracrystalline transport resistances and represents measuring conditions which are closest to the technical application. Supplying, in addition, the consortium with the inevitable equilibrium data of adsorption, this technique assumes a very central position within the consortium.

As illustrated in the General Introduction, the large variety of diffusion-related problems emerging in the literature of the last few years insistently points to the incessantly increasing relevance of the topic. These studies include sophisticated theoretical approaches [11-19] in need of their proof by adequately reliable experiments, challenging technological projects based on aspects of zeolitic diffusion [20-25], novel principles of diffusion measurement [26-29], diffusion anomalies [30-37] and an overwhelming number of "new" systems to be investigated [38-49], with the inherent risk of new misinterpretations as long as the "old" problems are still unsolved.

2.2. Own Activities in the First Period

The fabrication and optimization of the apparatus for the scheduled uptake and release experiments was in the centre of our activities. The device is based on a magnetic suspension balance (Rubotherm, Bochum), offering a time resolution of 0.8 s and temperature control with an accuracy of ± 0.1 K. Sample support was designed as a stack of metal plates, which simultaneously ensured mono-layer disposition of the zeolite crystallites and their thermal contact with an essentially infinitely large heat sink. In this way, the disturbing influences of bed diffusion and heat release on the overall processes were strived to be minimized [50]. In addition to adjustment to single-component diffusion studies, the use of the device may be extended to the application for uptake and release experiments with two-component gas mixtures. Further details of the apparatus and of the measuring procedure are published in [51, 52]

After completion of the device, diffusion measurements were commenced with selected n-alkanes (propane, n-butane, n-hexane) in zeolites NaCaA and with isobutane, n-butane and n-hexane in zeolites ZSM-5 and silicalite-1. Data analysis was performed on the basis of the non-isothermal sorption model following ref. [53]. Figs. 1 and 2 illustrate that the first results nicely fit into the general tendency observed for such systems: The diffusivities deduced from the (macroscopic) adsorption/desorption measurements are smaller than the data resulting from the microscopic techniques. Moreover, among the macroscopic techniques, they appear to yield the largest values. It has to be clarified in future studies whether the differences between the macroscopic techniques might be referred to differences in sample preparation, which may be of particular relevance for the formation of surface barriers.

Last not least, the activities within this project had to ensure a fast characterization of the synthesized materials distributed within the consortium with respect to their sorption capacities [54, 55].

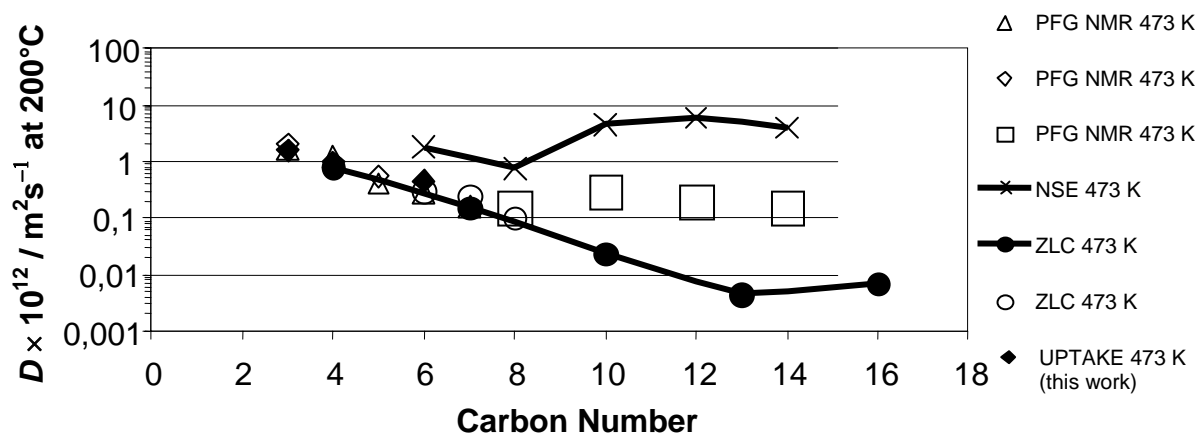


Fig.1. Diffusivities from uptake measurements for propane, n-butane and n-hexane on zeolite NaCaA compared with the results from other techniques at 473 K

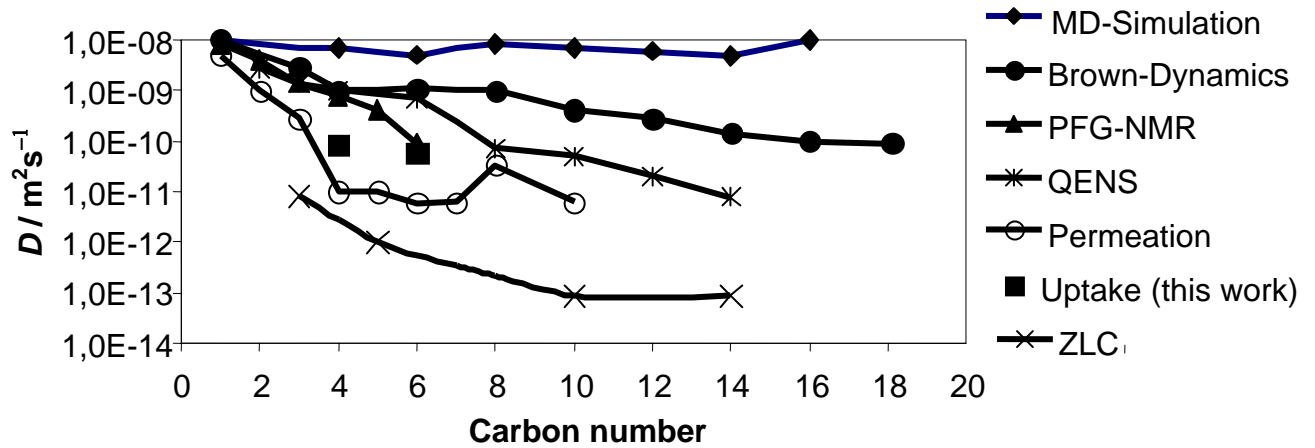


Fig. 2 Diffusivities from uptake measurements for n-butane and n-hexane on ZSM-5 compared with the results from other techniques at 300 K

3. Issues and Working Programme

3.1. Issues

The work of this project is devoted to the macroscopic measurement of the transport diffusivities in transient adsorption/desorption experiments (i. e. of macroscopically determined transport diffusivities) for comparison with the diffusivities of comparable systems obtained by the other techniques available in the consortium. Particular care is given to the investigation of the influence of as many parameters as possible, including loading and temperature as well as the nature (size, composition) and the pre-treatment conditions (activation, deterioration) of the zeolite samples, with the option of a deliberate change of the permeability of surface barriers.

In parallel to these activities, the consortium is supplied with equilibria data, i. e. the adsorption isotherms, inevitably needed for an estimate of the relative pore filling during the different measurement and thus for a first interpretation of the observed concentration dependencies. Moreover, in addition to the evidence provided by QENS [56], sorption isotherms permit the determination of the thermodynamic factor $\ln p(c)/\ln c$ inevitable for correlation equilibrium and non-equilibrium data of diffusion.

3.2. Working Programme

The experiments will be carried out using an equipment designed for volumetric-gravimetric measurements of co-adsorption equilibria of binary gas-mixtures. A schematic flow diagram of the equipment is sketched in Fig. 3. Details of the measurement technique, the used equipment and data handling are given in [51, 52, 57].

In a first step, the pure components of desired gas-mixture are prepared at pressures P_i^* and temperatures T_i^* , $i = 1,2$ in each of the evacuated storage vessels (SV). Masses of gas components m_i^* can be calculated by the thermal equation of state (EOS) $\rho_i^* = \rho_i^*(P_i^*, T_i^*)$ and the (known) volumes of the storage vessels V_{SV1} and V_{SV2} . Then the valve between two storage vessels (e. g. SV1 and SV2) is opened and a homogeneous gas mixture with known concentration is prepared using a circulation pump. Now the valve between the two storage

vessels and the adsorption chamber is opened and both components are adsorbed on the reactivated adsorbens. During the equilibration process data are measured continuously for a given time period and a complete data set (microbalance signal $\Delta m(t)$, pressure $P(t)$ and temperatures $T_i(t)$) is measured and recorded. Using the microbalance equation, the EOS with the measured data $P(t)$ and $T(t)$, the specific surface excess amount adsorbed of both components at any time t , $n_1(t)$ and $n_2(t)$, could be calculated.

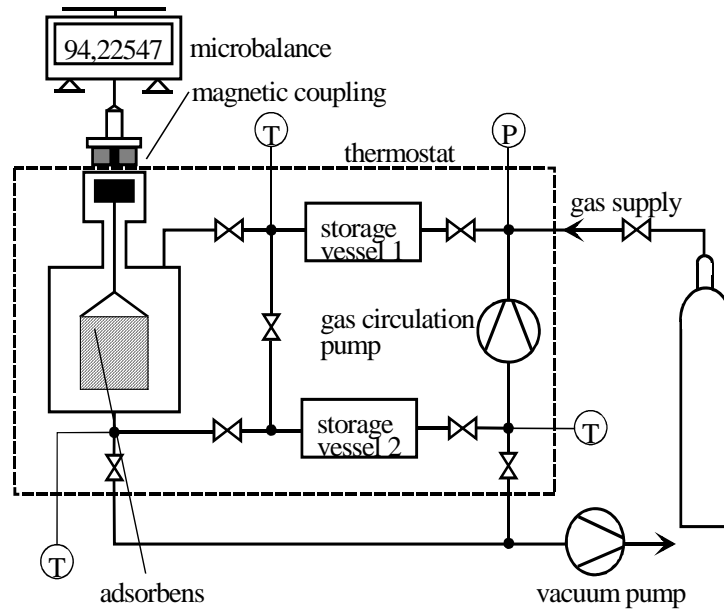


Fig 3 Schematic diagram of the volumetric-gravimetric measurement equipment.

By combining the:

- material balance of the components in the equipment before and during adsorption,
- microbalance equation,
- EOS, $Z(P,T,y_1)$, of the binary mixture,

the molar concentration of the adsorptive, $y_1(t)$ can be calculated from the measured data [51, 52, 57]. With these data, the specific surface excess of the constituents of the binary mixture, $n_1(t)$ and $n_2(t)$, can be determined. From these amounts adsorbed the molar concentrations of both components in the adsorbed phase, $x_1(t)$ and $x_2(t)$, could be observed. These data allow to investigate the equilibration process during adsorption of a binary gas mixture in detail, i.e., in particular

1. the equilibration of the adsorption of pure components on the reactivated adsorbens,
2. the two equilibration processes of a binary gas mixture, i.e. the partial uptake curves of each component,
3. the kinetic properties of each component in the mixture and
4. the (co- and counter-) diffusion coefficients of each component in the mixture.

Measurements can be performed for binary mixtures where the molar masses of both components are different.

After completion of this transient sorption device during the first period of support and after abolishment of artefacts in the performance of the measurements caused, in particular, by pressure instabilities, reliable uptake and release data for the systems of relevance for the consortium may be attained. This concerns in particular the following types of zeolites:

3.2.1. LTA

As one of the most intriguing results obtained during the first period of support, for n-alkanes in zeolite NaCaA notable deviations from a monotonic dependence of the diffusivities on the chain length has been observed [58, 59], in particular in the range from 7 to 12 carbon atoms. Upgrading and confirmation of this finding is among the main activities of the consortium, under particular emphasis of the macroscopic techniques, in order to discriminate up to which degree the observed tendencies are masked by surface resistances or comply with them. Hence, measurement with crystallites of deliberately varied surface properties are of particular relevance.

Further, diffusion studies shall be performed with sub-critical methanol vapor. Methanol in NaCaA was the first system, in which intracrystalline transport diffusion could directly be observed via interference microscopy [60, 61]. Moreover, due to the presence of the bivalent calcium ions in the zeolite bulk phase, the intracrystalline diffusivity of methanol as a polar molecule may be expected to be additionally slowed down, which might provide the option of reducing the relative influence of surface barriers.

Just contrary to that, in cation-free LTA a dramatic enhancement of the intracrystalline diffusivity should be observed. This should in particular concern the polar methanol molecules, so that their diffusivities should get closer to those of methane and ethane, as has been found already by preliminary PFG NMR studies [62]. In turn, owing to the enhanced intracrystalline diffusivities, better options for a detailed study of possible surface barriers are provided. Whether the relevant gravimetric studies may in fact be performed depends on the amount of cation-free LTA (and the crystal sizes) emerging from the efforts in zeolite synthesis.

3.2.2. Silicalite-1/ZSM-5

In contrast to zeolite NaCaA, the diffusivity of the n-alkanes in MFI-type zeolites was found to decrease monotonically with increasing chain length [63, 64]. There exist, however, studies by molecular modelling which, similarly as with zeolite NaCaA, predict oscillating diffusivities with (further) increasing chain lengths [11, 14, 23, 65]. Hence, further activities of the consortium shall be devoted to an enhancement of the range of chain lengths so far considered.

Again, the existence and quantification of possible surface barriers shall be in the focus of the studies. The evidence of such studies depends on the comparability of the measuring conditions of both the macroscopic and microscopic techniques. The latter ones notably improve with increasing temperatures so that it is vital to perform the measurements with the all-silica representative silicalite-1, to reduce the option of unwanted cracking reactions as observed with ZSM-5 [63].

In comparison with the n-alkanes, diffusion of branched n-alkanes and aromatics is notably reduced. While in the case of isobutane, still essentially all techniques of diffusion measurement are applicable (including PFG NMR with the option of MAS), the diffusion of longer iso-alkanes and the aromatics shall most likely be accessible by only the macroscopic techniques and IR- and interference microscopy. Both the practical impact of such studies and the option to directly trace the influence of compatibility ("commensurability") of channel architecture and molecular shape on diffusion [66-70] make such studies highly desirable.

3.2.3. *NaX*

Among all so far considered nanoporous materials, the large-pore zeolite NaX allows PFG NMR and QENS measurements over the largest spectrum of guest molecules, including in particular n-alkanes, branched alkanes, aromatics and methanol. Most interestingly, in previous studies only with methanol as a guest molecule [71, 72] macroscopic and microscopic studies revealed satisfactory agreement. The reconsideration of this problem, in particular for benzene/toluene as a standard molecule of previous studies [4, 5, 73-75] and for the n-alkanes is among the key issues of this project.

3.2.4. *Ferrierite*

Corresponding with the expenses for producing sufficiently large amounts of ferrierite crystallites with the properties necessary for interference and IR microscopy, macroscopic diffusion studies of this system shall be primarily performed by the (T)ZLC technique. It shall be decided during the course of these experiments, whether complementary gravimetric measurements are possible and strongly desirable.

3.2.5. *AlPO₄-5*

So far, clear and unambiguous experimental evidence on the occurrence of pure one-dimensional zeolitic diffusion in general, and of single-file diffusion in particular, is missing [76]. While in transient experiments one-dimensional (including single-file) diffusion does not yield any peculiarities in comparison with multi-dimensional diffusion, the situation is completely different in self-diffusion and counter-diffusion experiments. It is aspired that zeolite specimens with 1D channel structure, suitable for IR and interference microscopy studies, are provided in such an amount which would allow gravimetric measurements with the identical material. However, even with smaller crystallites, which would not suffice the requirements of IR and interference microscopy, comparative sorption and release experiments on the one side and counter-diffusion experiments on the other side are planned. Due to the confinement of molecular transport to one dimension, the observed interrelation should dramatically deviate from that in two- and three-dimensional pore networks.

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4. Requested Financial Support

4.1. Personnel

1 PhD student BAT IIa/2

for performing and analysing the gravimetric and volumetric-gravimetric experiments

1 Research Assistant (80 h/month)

for the routine measurement of adsorption isotherms

4.2. Durable Equipments

Pressure sensors (of ultra-high precision)

€2,500.-

Ultrahigh-precision pressure sensors are needed for accurate pressure measurements in the gaseous adsorptive because for both kinetic and equilibrium measurements of gas adsorption

the determination of the gas pressure is decisive for accuracy and reliability of data. The accuracy of the pressure sensor mainly determines the accuracy and quality of the experiments.

Data acquisition system	€2,500.-
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Kinetic sorption measurements lead to many experimental data which have to be handled, stored, transformed. In case of volumetric-gravimetric experiments, at the same time different data sets have to be collected and stored. In practice, this can only be achieved if an effective electronic system, i.e. a PC with special interfaces is at hand.

Gas circulator pump	€800.-
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Installations for measuring kinetic adsorption processes and/or gas adsorption equilibria normally consist of several vessels connected by proper tubing and augmented with valves. In order to ensure equalized pressure in all parts of the system and, in case of gas mixtures, also equal gas concentrations at any place, the sorptive gas must be circulated within the installation. To achieve this, the circulation pump is needed for providing a soft and controllable gas flow inside the adsorption system.

Gas storage vessel for volumetric part of apparatus	€1200.-
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4.3. Consumables

Sorptive gases (ultra-high purity, Air Liquide)	€ 6,000.-
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Delivery and handling of gas steel bottles	€ 1,500.-
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Valves, Sealings etc.	€ 3,500.-
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Computer & Printer Supply	€ 1,000.-
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4.4. Travelling

Implying that the group meetings are ensured by central funding the travelling budget has primarily to be used for keeping personal contact with other laboratories in the field of transient sorption measurement, in particular with Prof. Marco Mazzotti, ETH Zürich, and Dr. Matthias Thommes, Quantachrome Instruments and for conference participation (Annual German Zeolite Conferences, Conferences of the International Zeolite Association and Adsorption Association). Therefore, a total amount of 2000 €per year, corresponding to 6000 €for the total period of time, is requested for supporting visits and conference participation.

5. Requirements for the Success of the Application

5.1. Team Members

- a) PD Dr. R. Staudt (applicant)
- b) Prof. Dr. H. Papp
- c) Dr. Jörg Hofmann
- d) Dipl.-Ing. Ricardo Bazan
- e) Dipl.-Ing. (FH) Jörg Nitzsche

5.2. Cooperation with Other Scientists

The primary partners of cooperation are the members of the consortium. For special support and scientific exchange in the field of adsorption equilibria and transient adsorption measurements, cooperation with the following scientists is realized or planned:

Prof. D. M. Ruthven, U of Maine, Orono, Maine, USA (guest of the department as Humboldt laureate 2002)

Prof. D. D. Do, UoQ, Brisbane, Australia

Prof. Dr. O. Talu, Cleveland State University, Cleveland, Ohio, USA

Prof. C. L. Cavalcante Jr., Universidade Federal do Ceará, Brazil

Prof. A. Mersmann, TU München

Prof. J. U. Keller, Universität Siegen

Dr. M. Thommes, Quantachrome Instruments, Boynton Beach, FL, USA

5.3. Available Equipments

Installation for pure gas adsorption measurements

In the institute (INC) several gravimetric apparatuses for measuring pure gas adsorption equilibria are available:

2 apparatuses mainly consist of Sartorius Microbalances to measure adsorption equilibria of pure components in a wide temperature and pressure range.

2 apparatuses using a microbalance with magnetic suspension to measure adsorption equilibria and uptake curves of pure components in a wide temperature and pressure range.

1 apparatus using a microbalance with magnetic suspension to measure adsorption equilibria of organic components from carrier gas in a wide concentration and temperature range.

2 apparatuses to measure breakthrough curves.

Installation for mixture gas adsorption measurements

In INC several apparatuses for measuring mixed gas adsorption equilibria are available:

1 Volumetric apparatus with GC to measure multicomponent adsorption equilibria.

1 apparatus to measure multicomponent breakthrough curves.

1 apparatus using a microbalance with magnetic suspension to measure adsorption equilibria of mixed gases or vapours from a carrier gas.

1 Pilot plant to study technical adsorption processes.

Other instruments for characterization of porous materials are available at University of Leipzig.

5.4. Support from the Own Budget

From the budget of the institute (INC) an amount of about 3000 €per year may be used for ensuring the operating conditions of the equipments.

5.5. Further Prerequisites

The institute offers the working places for the co-workers, applied for, as well as the necessary laboratories. The infrastructure of the institute allows the use of the library, data-networks and computer systems free of charge.

6. Statements

6.1. Collaborative Research Centres (Sonderforschungsbereiche)

The present application cannot be part of any of the existing collaborative research centres of the University.

6.2. Application for Support by Different Sources

I have never applied for financial support of this or a similar project. If I shall do so, I will immediately inform the German Science Foundation (DFG).

6.3. Information to the University Representative of DFG (Vertrauensmann)

The university representative of the DFG has been informed about this proposal.

7. Signature

Leipzig, June 19, 2006

A handwritten signature in black ink, appearing to read 'R Staudt', written in a cursive style.

PD. Dr. Reiner Staudt