

Application for Extension of Financial Support of

**Project 3:  
ZLC and Tracer(T)-ZLC Diffusion Studies  
with Zeolites**

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

Prof. Dr. Stefano Brandani  
Department of Chemical Engineering  
University College London

Financial support requested from: EPSRC

# 1. General Information

## 1.1. Applicant

Prof. Dr. Stefano Brandani  
Professor in Chemical Engineering  
Born 07 January 1969  
Department of Chemical Engineering  
University College London  
Torrington Place  
London WC1E 7JE, UK  
Phone: 0044 20 7679 2315  
Fax: 0044 20 7383 2348  
E-mail: s.brandani@ucl.ac.uk  
-private address: 154 Woodhouse Road  
North Finchley  
London N12 0RP, UK  
phone: 0044 20 8445 1617

## 1.2. Topic

ZLC and Tracer(T)-ZLC Diffusion Studies with Zeolites

## 1.3. Code Word

Diffusion and self-diffusion by the ZLC method.

## 1.4. Research Areas

Material Sciences  
Chemical Engineering  
Physical Chemistry  
Interface Sciences

## 1.5. Scheduled Total Duration of Support

six years

## 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

The Zero Length Column (ZLC) and the Tracer ZLC (TZLC) methods yield the limiting transport diffusivities and the (tracer exchange) self-diffusivities that can be compared directly to microscopic techniques, such as PFG NMR and QENS, without the need for thermodynamic correction factors. Under appropriate experimental conditions it will be possible to measure also single-component adsorption isotherms. With the attained diffusivity data during the first period first important contributions have been made towards a database of diffusion results as an invaluable tool for the development of the understanding of molecular transport in microporous solids.

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

### **2.1. State of the Art**

The introduction of the ZLC technique in the late 80's by Eic and Ruthven [1, 2] offered an elegant and powerful method of macroscopic diffusion measurement with the exclusion of corruption by external transport resistances (like the so-called bed [3, 4] and valve [3, 5-7] effects) and the finite rate of heat release [3, 4, 8].

As the main result of the work within the first period of the application, with particular contributions by the ZLC technique, molecular transport in zeolites has been found to be subject to a hierarchy of transport resistances. As a consequence, for different observation scales 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. ZLC 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 [9-17] in need of their proof by adequately reliable experiments, challenging technological projects based on aspects of zeolitic diffusion [18-23], novel principles of diffusion measurement [24-27], diffusion anomalies [28-35] and an overwhelming number of "new" systems to be investigated [36-47], with the inherent risk of new misinterpretations as long as the "old" problems are still unsolved. As a part of this general tendency, the ZLC technique develops to a more and more popular method [42, 45, 48-53], in particular owing to the easy features of its application [2, 54, 55]. Most recently, the ZLC method has also been applied to trace surface modification of zeolite ZSM-5 [56].

### **2.2. Own Activities in the First Period**

The activities during the first period included methodological developments to make the range of chain lengths of the n-alkanes for ZLC diffusion studies with zeolites as large as possible, following one of the central issues of the research group. The success of these efforts is best documented for zeolite NaCaA where diffusion measurements for the whole homologous series from n-hexane till n-tetradecane could be performed [57]. Among others, the methodological progress in the measurements is based on the inclusion of back-pressure regulation to stabilize the flux to the flame ionization detector applied for analysing the ZLC efflux.

In complete agreement with the other techniques of the group, the steep decay of the diffusivities with increasing loading has been found to be stopped - if not even reversed - at chain lengths of about eight to ten hydrocarbons [58-60]. In contrast to the behaviour with NaCaA, for MFI-type zeolites the diffusivities were found to decrease monotonically over the whole range of chain lengths [61, 62], similarly as - so far mainly observed by PFG NMR - in zeolite NaX[63]. This tendency may be correlated with the fact that zeolite LTA disposes of a

pore structure with pronounced windows between the individual cages [64] which neither in MFI nor in zeolite NaX do exist in such a prominent way. Obviously, in a pronounced cage structure, with increasing chain lengths molecular propagation may again become faster, if there is a tendency that the molecules prefer to reside with their chain ends in adjacent cages rather than in one and the same.

As a general tendency of all these measurements, in both NaCaA and MFI the macroscopic diffusivities were found to be smaller than the corresponding microscopic techniques. As a crucial experiment for exploring the origin of this difference, partial-loading experiments have been performed [57, 65]. For all considered systems, molecular desorption after "partial loading" was observed to fade initially at a much higher rate than to be observed after final equilibration. This indicates a non-uniform sorbate concentration over the crystallites at partial loading so that, at least for the thus investigated systems, a dominating influence of surface barriers can be excluded. Hence, the most plausible explanation of the observed difference between the macroscopic and microscopic measurements were the existence of internal barriers with spacings too large to be observed by QENS and on the limit to be traced by PFG NMR [66-70].

Further diffusion-related activities during the first period of application were devoted to the establishment of a novel measuring principle for diffusion in nanoporous materials based on the interference of sound propagation and molecular migration [71, 72] and to the evaluation of pressure cycling technologies [73].

### **3. Issues and Work Programme**

#### **3.1. Issues**

The work of this project is devoted to the determination of the diffusivities resulting from ZLC experiments, i.e. of macroscopically measured self-diffusivities by TZLC and macroscopically measured limiting transport diffusivities by standard ZLC, for comparison with the diffusivities of comparable systems obtained by the other techniques available in the consortium. Following the outcome of previous studies, during the first period of the application also the systematic comparison of different techniques for n-alkane diffusion in zeolites NaA and silicalite-1 led to the result that generally the macroscopically determined diffusivities were notably smaller than the microscopic data. Since, on the other hand, partial loading experiments with selected samples exclude a dominating influence of surface barriers, the diffusivities appearing from the ZLC studies have to be referred to the influence of internal transport barriers. The quantification of these barriers in zeolites NaCaA and silicalite-1 (as well as their consideration in NaX) in accordance with the output of all the other techniques will be in the very centre of the future activities.

Further, again in agreement with the consortium partners, ZLC measurements will as well be performed with the special zeolite types ferrierite and MFI which - differing from the so far considered three-dimensional pore network - offer the option of diffusion measurement in lower dimensions. Since crystal specimens of ideal habit - if at all - will only be available in rather small amounts (down to a few crystals only, which were already sufficient for IR and interference microscopy) ZLC, which, as the most sensitive macroscopic technique being able to operate with a few milligrams only, is particularly suited for such studies. Particular care is given to attain such experimental conditions, including loading and temperature as well as the nature (size, composition) and the pre-treatment conditions (activation, deterioration) of the

zeolite samples, which allow direct comparison with or, at least, extrapolation to the results of the other techniques. Following the procedure of tracer ZLC measurements, the technique shall be further developed to observe counter-diffusion phenomena

In parallel to these activities and complementing the information provided from project 2 on adsorption isotherms and from project 7 on thermodynamic factors, experiments under low flow rate conditions will be carried out to measure adsorption isotherms. They are needed for both zeolite characterization and for an interpretation of the correlation between (genuine) equilibrium and non-equilibrium diffusivities.

### **3.2. Working Programme**

After development and completion of the device for ZLC and tracer ZLC measurement and confirmation of its performance by first systematic studies of the chain-length dependences of the n-alkane diffusivities in NaCaA and ZSM-5/silicalite-1, the application of the technique shall be optimized with respect to a maximum output of possibilities to correlate the results with those of other techniques within the consortium. 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 [59, 74], 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, measurements with crystallites of deliberately varied surface properties are of particular relevance. Since - on the other hand - the findings of ZLC experiments with partial loading point to internal mass resistances rather than to surface barriers as the main reason for the differences between microscopic and macroscopic techniques, the confirmation and quantification of assumption requires particular care. As a part of this issue, it has to be clarified why all so far applied techniques (QENS, PFG NMR and ZLC) reveal different patterns (and chain lengths) for the deviations from a monotonic decrease of the diffusivities with increasing chain lengths.

Further on, 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 [75, 76]. 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 [77]. 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.

Methodological developments towards an application of ZLC to multicomponent diffusion studies shall include measurements of mixtures of small chain length (ethane, propane) and large chain length (n-hexane) n-alkanes. Following both the general predictions of irreversible thermodynamics [3] and the application of the Maxwell-Stefan formalism to zeolites [78, 79] in this case correlation between the single- and two-component diffusivities can be expected to be mainly mediated by the thermodynamic factor rather than by micro-kinetic correlations.

### 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 [62, 64]. There exist, however, studies by molecular modelling which, similarly as with zeolite NaCaA, predict oscillating diffusivities with (further) increasing chain lengths [9, 12, 21, 80]. Hence, further activities of the consortium shall be devoted to an enhancement of the range of chain lengths so far considered.

Most importantly, the ZLC experiments with n-alkanes in MFI-type zeolites of the first period revealed an even much more pronounced reduction of the diffusivities in comparison with the microscopic techniques than observed with NaCaA. Since again the partial loading experiments point to internal mass resistances rather than to surface barriers as the origin of these differences, the confirmation and quantification of this assumption requires particular care. The much stronger effect in comparison with NaCaA is in agreement with the finding of PFG NMR studies, where for ZSM-5/silicalite-1 pronounced indications of such barriers have been observed, while so far there are only first tentative indications for the existence of such barriers in zeolite NaCaA (see section 3.1.1 of project 6).

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 [64].

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 [81-85] make such studies highly desirable.

In contrast to NaCaA, multicomponent diffusion studies with mixtures of small chain length (ethane, propane) and large chain length (n-hexane) n-alkanes should reveal correlations between single-component and multicomponent diffusion on the one hand, and between transport and self-diffusion on the other, which include the influence of both (equilibrium) thermodynamics and molecular kinetics. Following either irreversible thermodynamics [3] or its extension by the Maxwell-Stefan formalism [78, 79], the influence of microkinetics, in addition to the omnipresent influence of the "thermodynamic factor", on the correlation

between the different diffusivities may be rationalized as a consequence of the mutual hindrance of the molecules during propagation in the intersecting channels of the pore system. By contrast, in zeolite NaCaA molecular propagation is controlled by jumps between adsorption sites (cavities) where - at least for not too high loadings - the jumps of different molecules occur independently from each other.

### 3.2.3. *NaX*

Among the nanoporous materials considered so far, 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 [86, 87] macroscopic and microscopic studies revealed satisfactory agreement, while - by contrast - for benzene/toluene discrepancies of up to two orders of magnitude have been observed [88]. With increasing loading, however, the observed difference (increasing TZLC data, decreasing PFG NMR data) was notably reduced. The reconsideration of this problem, in particular for toluene/benzene as standard molecules of previous studies [3, 89-92], under particular reconsideration of the respective concentration dependencies, and for the n-alkanes, is among the key issues of this project.

### 3.2.4. *Ferrierite*

The ZLC and TZLC techniques shall be essentially the only macroscopic methods which are definitely scheduled to be applied for diffusion studies with ferrierite. This is due to the fact that the ferrierite crystals offering unprecedented options for diffusion measurement by interference microscopy will probably not be available in amounts necessary for the application of the other macroscopic techniques. As a particular structural feature, the so far synthesized specimens dispose of 8-membered ring channels which are accessible on both crystal sides, while the entrance to the larger (10-membered ring) channels are on both sides blocked. With methanol as a guest molecule, these crystals have proven to be excellent candidates for separately determining surface barriers and intracrystalline (transport) diffusivities over the total range of concentrations, so that the investigation of the interplay of intracrystalline diffusion and surface resistances by a macroscopic technique is an attractive task for the future. Moreover, if the efforts of the synthesis groups to find routes to a deliberate variation of the accessibility to the two different types of channels shall be successful, ferrierite may as well turn out as an ideal model host for the investigation of single-file diffusion (via switching the accessibility from the small to the large channels) [93] and for molecular traffic control [94-96].

### 3.2.5. *AlPO<sub>4</sub>-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 [93]. 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. In addition, 1D host systems provide ideal conditions for the application of interference and IR microscopy which have been shown to provide the most direct evidence on intracrystalline transport phenomena. Though 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, the attempts may fail and in this case the (T)ZLC technique would again be the only applicable macroscopic technique. Moreover, for special surface preparations (T)ZLC shall turn out to be the method of choice among the macroscopic techniques, owing to its easy use, its versatility and the extremely modest requirement (down to milligrams) of zeolite material to be applied.

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## **4. Financial Support**

secured by EPSRC

## **5. Requirements for the Success of the Application**

### **5.1. Team Members**

- a) Dr. Stefano Brandani (applicant)
- b) PhD student

### **5.2 Cooperation with Other Scientists**

The primary partners of cooperation are the members of the consortium.

### **5.3. Available Equipment**

- Two ZLC systems with FID and TCD detectors
- Two quadrupole mass spectrometers for tracer and multicomponent experiments

### **5.4. Support from Own Budget**

Full support is sought from the EPSRC.

### **5.5. Further Prerequisites**

Laboratory space will be made available and training for the PhD student provided. The infrastructure at UCL will provide for access to data-networks and computer systems.

## **6. Signature**

London, June 19, 2006

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

Prof. Dr. Stefano Brandani