Diffusion of Isobutane in ZSM-5 Zeolite: A Comparison of Quasi-Elastic Neutron Scattering and Supported Membrane Results

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Isobutane diffusivities in ZSM-5 zeolite have been measured by quasi-elastic neutron scattering (QENS) and supported membrane techniques. This is the first diffusivity measurement of a branched alkane inside a zeolite of MFI type using a microscopic method. The self-diffusion coefficient derived from QENS is 3×10^{-12} m^2/s at 500 K. The diffusivity obtained with the supported membrane is 1 order of magnitude larger. In view of the large differences usually reported in the literature between microscopic and macroscopic techniques, the comparison between QENS and supported membrane data is quite satisfactory. The activation energy for diffusion determined from QENS is 17 kJ/mol. Because of the variation of loading due to temperature changes, an apparent activation energy is obtained with the supported membrane; it is 34 kJ/mol. In this zeolite, the diffusion of branched hydrocarbons is much slower than that of linear alkanes; the diffusion coefficient of isobutane is found to be 3 orders of magnitude lower than that of *n*-butane by QENS.

1. Introduction

The use of ZSM-5 zeolites is widely recommended for adsorption separation processes mainly in the field of refining and for gas processing. One of the most promising applications of ZSM-5 zeolites is the kinetic separation of alkane isomers for upgrading the octane number of gasoline. This separation is based on the differences in diffusion coefficient of the various isomers in the zeolite. Considering the pore size of this zeolite (∼5.5 Å) and the diameter of alkane molecules, it is likely that large steric effects will occur during adsorption and diffusion. Despite the large number of published papers, the diffusion properties of molecules with kinetic diameters close to those of the zeolite channels still have not been clearly elucidated. The literature has mainly focused on *n*-alkane diffusion, and various techniques were applied (molecular dynamics simulation, microscopic measurements, and macroscopic measurements).[1−18] The self-diffusion coefficients derived from molecular dynamics simulations or microscopic methods are usually much larger than the transport diffusion coefficients obtained from macroscopic techniques. Such is the case for linear alkanes in MFI type zeolites as reported by Kärger and Ruthven.[19] The two microscopic methods are quasi-elastic neutron scattering (QENS) and pulsed-field gradient NMR (PFG NMR). Much less work was carried out for branched alkanes, though several papers concerning the membrane approach have been published. Two studies have been reported for silicalite single crystals by Hayhurst and Paravar[1] and Shah et al.[12] Kapteijn and co-workers[14,15] and Funke and co-workers[20−22] have used supported membranes.

We report here measurements of micropore diffusion coefficients of isobutane in ZSM-5 zeolite using two different experimental techniques: QENS and the supported membrane method. This has been made possible because of recent developments in the synthesis of tubular membranes of high quality.[23] This is the first time that a combination of microscopic and macroscopic techniques has been used to study the diffusion of a branched alkane in the MFI structure.

2. Experimental Section

2.1. Membrane Technique. The advantage of the membrane technique is that the system is not affected by finite heat transfer because measurements are made under steady-state conditions.

Membrane. Details of the hydrothermal synthesis have been described previously.[23] The support is a multilayer porous tube (purchased from SCT-US Filter, type Membralox Ti 70). From the inside to the outside of the support, there are three alumina layers with different pore diameters. The smallest one has a nominal average pore diameter of 0.2 μm. The zeolite grew inside the inner alumina layer, which is ∼20 μm thick. It has been found that there is no mass transport limitation inside the two other alumina layers. The membrane was checked by measuring the 1,3,5-triisopropylbenzene permeation (the kinetic diameter of this molecule is 7.4 Å). It was shown that no permeation of this molecule occurred, indicating that there are no cracks in the membrane.

Experimental Set up. Gas fluxes were regulated by mass flow controllers. Feed and permeate, which could be in cocurrent or countercurrent configurations, were analyzed by a Varian gas chromatograph (Star 3400CX) with an FID detector. The pressures on the feed side and the permeate side were detected separately by two standard pressure gauges (Keller OEM, range 0−20 bar), whereas the pressure difference between these two sides was monitored by a differential pressure gauge (Effa GA

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63/64, range 0−3 bar) with a pressure regulator (Brooks model 8606). The temperature was controlled with thermocouples and monitored with three furnaces in order to avoid temperature gradients. Permeation experiments were performed with one gas: isobutane (purity 99.95).

Measurements. The membrane was previously heated at 673 K for 12 h using helium gas in order to remove any adsorbate or template traces. The sample was then cooled to room temperature and isobutane introduced. Constant pressures were maintained on both the feed side and the permeate side. This provided a simple and convenient way of measuring the flux. The measurements were made under steady-state conditions and with no concentration gradient along the surface of the membrane. Several hours were necessary to obtain a fixed value of the flux at low temperatures.

2.2. QENS Measurements. The neutron experiments were performed on the new backscattering spectrometer IN16 at the Institute Laue-Langevin in Grenoble, France. This spectrometer improves both the neutron flux and the energy resolution over existing backscattering spectrometers by applying focusing techniques. By use of unpolished Si(111) crystals as analyzers, the line shape of the energy resolution function is close to a Gaussian with a width of about 0.45 μeV, half-width at half-maximum (hwhm). In this work, small broadenings of the resolution function, due to long-range translation, are measured. Therefore, great care was taken to reproduce the shape of the resolution function, using a sum of Gaussians. With this procedure, broadenings of only 10% of the resolution could be safely resolved. The energy transfer, $\hbar\omega$, was analyzed in a window of ± 12 μeV. The momentum transfer, $\hbar Q$, depends on the scattering angle; in our experiment the Q range was 0.16−1.5 Å^{-1}.

For the QENS experiment, the ZSM-5 crystals had a Si/Al ratio of 36. The zeolite was activated by heating to 770 K under flowing oxygen. The sample (3 g) was cooled and pumped to 10^{-4} Pa while heating again to 770 K. After cooling, isobutane was adsorbed at a given pressure onto the pretreated zeolite. The adsorbed quantity corresponds to three molecules per unit cell. The sample was transferred inside a glovebox into a cylindrical aluminum container of annular geometry. A similar cell containing the same amount of dehydrated zeolite was also prepared.

The neutron containers were placed in a cryofurnace, and measurements were performed at 450, 500, and 570 K. The scattering from the dehydrated zeolite was subtracted from the spectra, which were recorded with the sample containing isobutane, after appropriate corrections from absorption and normalization.

3. Theory

3.1. Membrane Technique. Diffusion of one adsorbed molecular species along a surface within the adsorbent pores can be considered in developing a very simple formulation for diffusion in a microporous medium. It is assumed that diffusion in the pores is the rate-determining process and that the other steps such as adsorption and desorption are so fast that they can be considered to be at equilibrium. So let us write the generalized Maxwell−Stefan (GMS) equations in a manner analogous to diffusion in bulk fluid phases[24−26] following Krishna:[27,29]

$$-\frac{\theta_i}{RT}\nabla\mu_i = \sum_{\substack{j=1\\ j\neq i}}^{n+1}\frac{\theta_j N_i - \theta_i N_j}{c^{\mathrm{sat}}\rho D_{ij}} \qquad i = 1, 2, ..., n+1 \tag{1}$$

where $-\nabla\mu_i$ is the chemical potential of species i, which is the driving for diffusion. N_i is the flux through the ZSM-5 membrane of component i. ρ is the density of the ZSM-5 zeolite, and c^{sat} represents the total concentration in zeolite. The coefficients D_{ij} express the GMS diffusivity. They reflect the facility for exchange between sorbed species i and vacant sites j. θ_i represents the fractional occupancy of the sites by the adsorbed species i, θ_{n+1} is the fraction of unoccupied sites, and θ_{t} represents the fractional occupancy of the sites by all the adsorbed molecules:

$$\theta_{n+1} = 1 - \theta_1 - \theta_2 - ... - \theta_n = 1 - \theta_{\mathrm{t}} \tag{2}$$

One peculiarity of diffusion in a microporous medium that is distinct from bulk fluid phase diffusion is that, since the total number of sorption sites is fixed, we always have equimolar counterdiffusion in the two-component system under consideration:

$$N_{n+1} = \sum_{i=1}^{n} N_i \tag{3}$$

This means that the vacancy flux balances the isobutane flux.

By analogy with the definition of the Knudsen diffusivity, Krishna[27,29] defined the Maxwell−Stefan diffusivities as

$$D_{i\mathrm{V}} = \frac{D_{i,n+1}}{\theta_{n+1}} \tag{4}$$

Assuming equilibrium between the surface and the sorbed phase, we have the following relationship for the surface chemical potential μ_1 of isobutane:

$$\mu_1 = \mu_1{}^0 + RT\ln(p_1) \tag{5}$$

where $\mu_1{}^0$ is the chemical potential in the chosen standard state and p_1 the isobutane pressure in the gaseous phase in equilibrium with the sorbed phase. Considering single-file diffusion of isobutane, the driving force on the left side of eq 1 can be rewritten in terms of the gradients of the fractional coverages:

$$\frac{\theta_1}{RT}\nabla\mu_1 = \Gamma\nabla\theta_1 \tag{6}$$

where we have defined a thermodynamic factor Γ as

$$\Gamma = \theta_1\frac{\partial \ln p_1}{\partial\theta_1} \tag{7}$$

Using eqs 1 and 6, one obtains

$$-\frac{\theta_1}{RT}\nabla\mu_1 = -\Gamma\nabla\theta_1 = \frac{N_1}{c^{\mathrm{sat}}\rho D_{1\mathrm{V}}} \tag{8}$$

The porosity of the smallest support layer, ϵ, is used to correct for the fraction of the membrane area that is not available for permeation owing to the presence of the alumina support. The isobutane flux through the zeolitic membrane, N, becomes

$$N = \epsilon N_1 = -c^{\mathrm{sat}}\rho\epsilon\Gamma D_{1\mathrm{V}}\nabla\theta_1 \tag{9}$$

To simplify the equation, we note $D_{1\mathrm{V}}$ as D. This coefficient is the counterdiffusion coefficient reflecting the facility for exchange between sorbed isobutane and vacant sites.

Knowledge of the adsorption isotherm[29] defines the relationship between the isobutane pressure p_1 and the surface occupancy θ_1, which is used to calculate Γ.

3.2. QENS. After subtraction of the scattering from the dehydrated zeolite, the intensity scattered by isobutane can be analyzed only in terms of hydrogen motions because of the large incoherent cross section of the hydrogen atom. The intensity scattered by the sample is proportional to the incoherent scattering function, $S(\mathbf{Q},\omega)$, where $\hbar\omega$ is the neutron energy transfer and $\hbar\mathbf{Q}$ the momentum transfer. Only the translational motion has to be considered in this work because rotational and vibrational motions involve much larger energy transfers (in other words, these motions are much faster).

In our previous work on the diffusion of linear alkanes in the MFI structure,[11,30,31] the jump diffusion model of Singwi and Sjölander[32] was found to describe accurately the broadenings of the elastic peak in the whole momentum transfer range. In this model, the molecule remains on a given site (or in a region of space of deep potential) during a time τ_0 and then diffuses during a time τ_1 until it is trapped again in a new equilibrium position. In our case, the time taken for the jump can be neglected ($\tau_0 \gg \tau_1$) so that the scattering function is a Lorentzian function with an hwhm corresponding to

$$\Delta\omega = \frac{1}{6\tau_0}\frac{\langle l^2\rangle Q^2}{1+\langle l^2\rangle Q^2/6} \tag{10}$$

where $\langle l^2\rangle$ is the mean-square jump length. A diffusion coefficient can then be calculated using Einstein's equation

$$D = \frac{\langle l^2\rangle}{6\tau_0} \tag{11}$$

At small Q values, corresponding to translation over distances larger than one unit cell, the broadening reduces to Fick's law, $\Delta\omega = DQ^2$, so that the value of the diffusion coefficient is not model-dependent. When the broadenings were fit at larger Q values, the mean jump distance and the residence time τ_0 can be determined so that another value of the diffusion coefficient can be obtained. Both values of the diffusion coefficient are usually in agreement within 20%.[30]

4. Results

4.1. Membrane Technique. Several permeation curves at different hydrocarbon pressures in the feed fluxes were measured as a function of temperature. Representative experimental curves for isobutane are presented in Figure 1.

Between 300 and 425 K, the isobutane permeation fluxes decrease slowly. The interpretation of this behavior is still unclear. It can be related to the first peak of the temperature-programmed-equilibration curve, which was assigned to a second type of adsorption site.[29] Possible effects from phase transitions from either the framework or the adsorbed phase can be envisaged. After 425 K, the flux increases for increasing temperatures, passes through a maximum at 600 K, and then decreases. This behavior is significant of the competition between the adsorption, which is decreased by increasing temperature, and diffusion, which is decreased by decreasing temperature. In previous experiments, isobutane diffusivities had not been measured at such high temperatures in ZSM-5 zeolite. It can be noted that the permeation curve at 1.5 bar in the feed side is similar to that obtained at 1.7 bar. The number of sorbed molecules per unit cell of zeolite on the feed side and the permeate side is given in Figure 2, and it is derived from the adsorption isotherms.[29] From Figures 1 and 2, we can observe a change in the different curves when the filling is about 4 molecules per unit cell. As already reported,[33,34] the number 4 is a magic number for the MFI type zeolite. From these results, the generalized Maxwell−Stefan approach is used to estimate the diffusivity of isobutane.

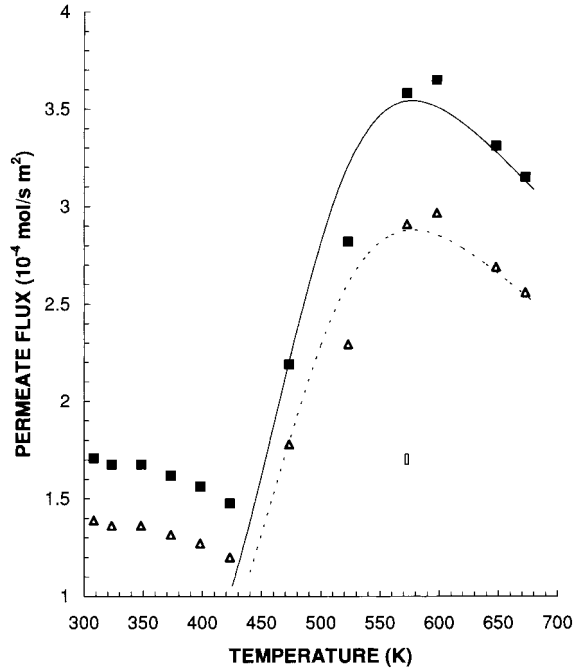

Figure 1. Permeation fluxes for isobutane as a function of temperature for feed pressures of 1.7 bar (■) and 1.5 bar (△) through a ZSM-5 membrane. The calculated and experimental data are compared above 430 K.

TABLE 1: Isobutane Diffusivities in ZSM-5 Zeolite

technique temp (K)	QENS D (10^{-12} m^2/s)	membrane (P_{feed} = 1.7 bar) D (10^{-11} m^2/s)
673		23.8
648		21.9
598		12.1
573		8.2
570	5.5	
523		3.6
500	3.0	
473		2.4
450	2.1	
423		0.9
398		0.9

The Maxwell−Stefan diffusivities (Table 1) are plotted as a function of the reciprocal temperature in Figure 3. The experimental error on the value of the diffusivities is a factor of 3. The diffusivity exhibits a good linear trend between 425 and 700 K. The calculated value of the diffusion activation energy is similar for the two differential pressures; it is of 34 kJ/mol.

The calculated curves and the experimental values of permeate fluxes are compared in Figure 1. They are in very good agreement.

4.2. QENS. The broadenings of the elastic peak measured for isobutane in ZSM-5 zeolite are very small, in fact much smaller than those observed for long linear alkanes, C_8−C_{14}, in the same zeolite.[35] This indicates a lower mobility for isobutane. A QENS spectrum obtained at 570 K is shown in Figure 4. The width of the experimental spectrum is only ∼15%

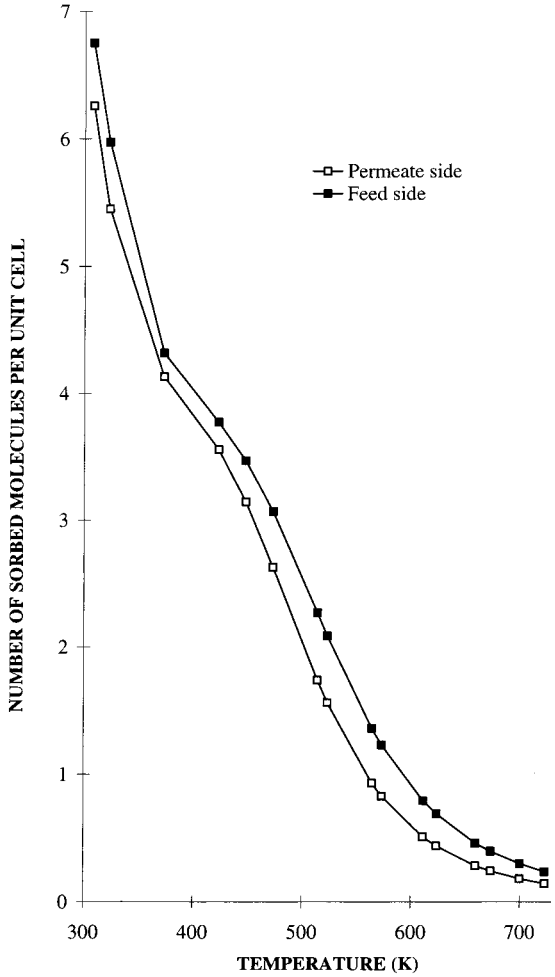

Figure 2. Number of sorbed isobutane molecules per unit cell of zeolite on each side of the membrane as a function of temperature (feed and permeate pressures are equal to 1.7 and 1 bar, respectively).

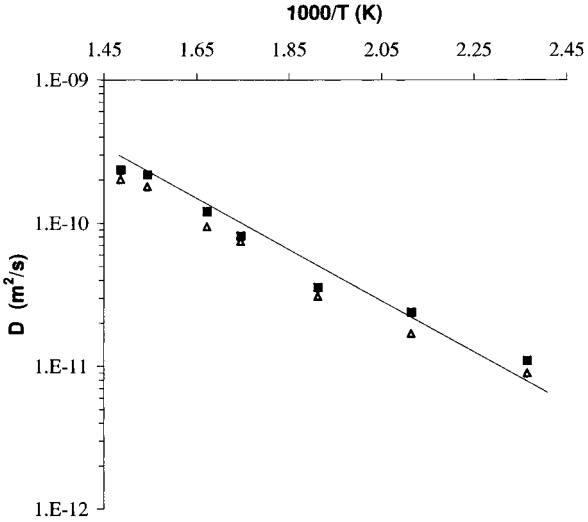

Figure 3. Arrhenius plot of the diffusion coefficient for isobutane through a ZSM-5 membrane for feed pressures of 1.7 bar (■) and 1.5 bar (△).

larger than the resolution function. The variation of the broadening as a function of Q^2 is shown in Figure 5, after fitting the spectra individually. The values of the broadenings for the spectra measured at small Q values were too small to be determined. With the spectrometer setup used, one is at the limit of the resolution for this system. However, all the spectra could

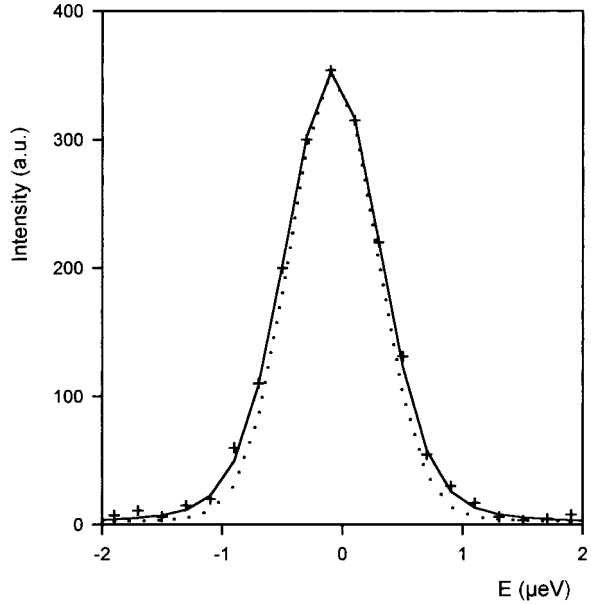

Figure 4. Comparison between experimental (+) and calculated (full line) QENS spectra obtained at 570 K for isobutane in ZSM-5 zeolite (three molecules per unit cell, $Q = 0.87$ Å^{-1}). The dotted line represents the resolution function.

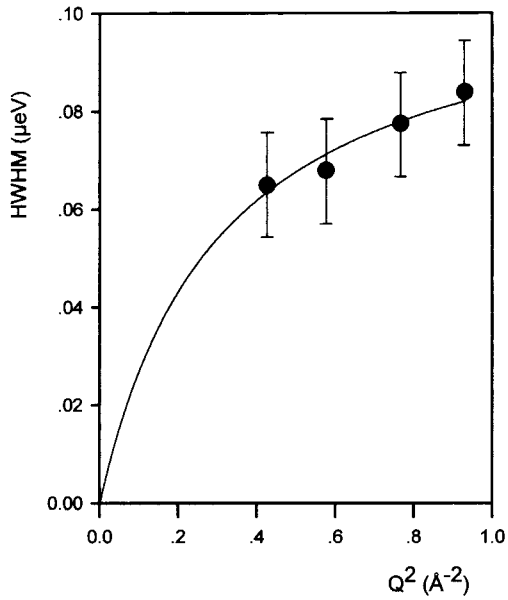

Figure 5. Broadenings derived for isobutane adsorbed in ZSM-5 zeolite at 570 K: (●) individual fits of the QENS spectra; the full line corresponds to a simultaneous fit with all spectra, using a jump diffusion model.

be fitted with the jump diffusion model, eq 9. The full line in Figure 5 shows the broadening behavior that is expected for this model. The two adjustable parameters, $\langle l^2 \rangle$ and τ_0, were refined from the spectra. The mean jump distance is 4.5 Å, and the mean residence time is 6 ns. Since there are no experimental points at low Q, the error on the value of the jump distance could be as high as a factor of 2, even if the error bars on the individual spectra are much smaller. Therefore, the error on the values of the diffusion coefficients given in Table 1 is a factor of 4, which is much larger than the usual error, ~50%.[11,30,31]

The broadenings measured at lower temperatures were smaller so that the value of the activation energy, which is derived from the QENS data, 17 kJ/mol, is only an estimate.

5. Discussion

Large discrepancies between microscopic and macroscopic diffusion coefficients are often reported so that the values obtained for isobutane in ZSM-5 zeolite from QENS and supported membrane techniques are considered to be in reasonable agreement. The diffusivities derived from QENS are about 1 order of magnitude lower, but in fact the data overlap if one takes into account the large experimental errors. The similarity of the values of the diffusivities obtained from the two methods indicates that the self-diffusion coefficient measured with a microscopic technique and the Maxwell−Stefan diffusivity are comparable quantities.

From QENS measurements, it is found that the self-diffusion coefficient of isobutane in ZSM-5 zeolite is about 3 orders of magnitude lower than the one of *n*-butane in the same zeolite.[11] Additional experiments were performed with 3-methylpentane; no broadening could be measured with the crystal setup used in this work, so the diffusivity is lower by a factor of 5 (at least) compared with isobutane. This is in agreement with results obtained with the supported membrane technique;[36] the diffusivity of 3-methylpentane is 1 order of magnitude lower than the one of isobutane.

The activation energies for diffusion derived from the two techniques show a discrepancy of a factor of 2. Apart from the large experimental errors, one should consider that the membrane value is, in fact, an apparent activation energy because the concentration of isobutane decreases with increasing temperature (from 4 to 0.2 molecules per unit cell), whereas the QENS measurements are performed at a fixed loading of three molecules per unit cell.

Our isobutane diffusion coefficients are difficult to compare with literature because most of the previous studies[1,10,12] were made at low temperature, between ambient and 400 K. In this temperature range, the adsorption of isobutane in ZSM-5 zeolite or in silicalite exhibits a second adsorption step according to both TPE[38] and isotherms results[29] (see also the recent paper by Zhu et al.).[39] The permeation flux has a strange behavior at low temperatures (Figure 1) so that the diffusion cannot be easily modeled in that range. Therefore, our results can be compared with only two other studies. The first one was made by Chiang et al. using concentration pulse chromatography (CPC).[37] Their data at 473 K are 3 orders of magnitude lower than the QENS values and 4 orders of magnitude lower compared with the membrane results. Another study was performed by Hufton and Danner, also using CPC.[9] At 423 K, they obtained a diffusion coefficient of 1.3×10^{-11} m^2/s, a value that is in very good agreement with the supported membrane technique data. Their activation energy, 24 kJ/mol, is between the values derived from QENS, 17 kJ/mol, and supported membrane methods, 34 kJ/mol.

It can be noted that the diffusivity of isobutane in ZSM-5 could not be measured by PFG NMR because of the short value of the transverse relaxation time, T_2.[40] Furthermore, the diffusion of *n*-butane and isobutane in silicalite was recently simulated at 300 K by molecular dynamics,[41] but the average values of the diffusion coefficients of the two isomers differ much less when compared with experimental results. This indicates that the model for the simulations is too simple, e.g., the united atoms potential, to describe the motion of branched alkanes with sufficient accuracy.

5. Conclusion

The diffusion of a branched alkane in ZSM-5 zeolite has been measured using a microscopic and a macroscopic method. Isobutane diffusivities derived from QENS and supported membrane techniques are in reasonable agreement. The self-diffusion coefficient of isobutane obtained by QENS is 3 orders of magnitude lower compared with *n*-butane. Considering that isobutane is the simplest branched alkane molecule, the diffusion of more complex branched alkanes should be even more restricted. Preliminary measurements performed with several branched alkanes support this view.

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