On the Translational Mobility of Benzene adsorbed on NaX-type Zeolites

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Application of the NMR pulsed field gradient technique and of quasi-elastic neutron scattering to molecular self-diffusion studies of benzene in zeolite NaX leads to coinciding results in both the absolute values and the concentration dependence.

The introduction of the NMR pulsed field gradient technique to adsorbate–adsorbent systems[1] revealed substantial differences in the coefficients of intracrystalline zeolitic diffusion in comparison with the results of traditional adsorption/desorption methods.[2] Since this time, the clarification of the correct order of magnitude of the translational mobility of molecules adsorbed within the intracrystalline pore system of zeolites is one of the most controversially discussed topics in zeolite research.[3,4] For several systems a critical re-examination of the earlier sorption data showed that the effects of external heat and mass-transfer resistances in limiting the sorption rates were far greater than originally assumed.[3,5—7] Taking account of these influences, in many instances reasonable agreement between sorption and NMR data could be obtained.[2,4,7—9]

However, there is also a number of well-documented experimental studies showing differences of up to two orders of magnitude.[4,8,10] Offering good measuring possibilities for
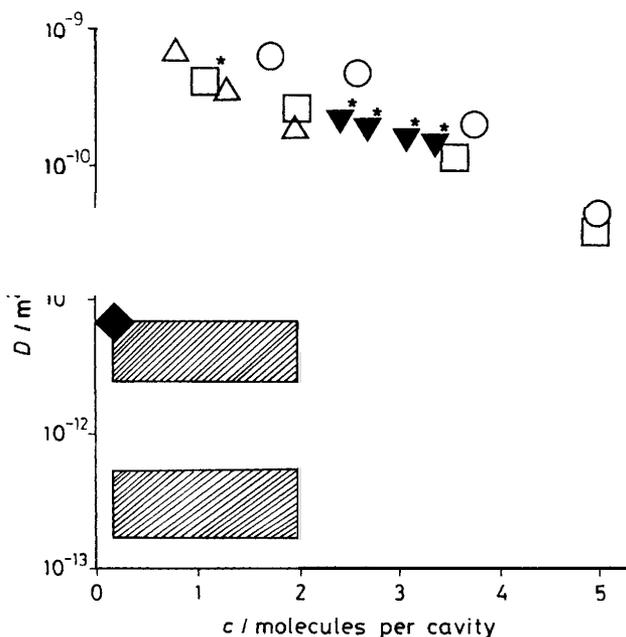

Figure 1. Comparison of the self-diffusion coefficients of benzene in zeolite NaX at 458 K directly determined by NMR pulsed-field-gradient measurements (O [17]; □ [8,18]) and quasi-elastic neutron scattering (△, this work), with the corresponding quantities ('corrected' diffusivities) determined from non-equilibrium measurements [▼, piezometric (constant volume)[11]; ◆, zero length column (ZLC) method[12,10]; hatched area, region of the results of gravimetric measurements with two different specimens[8]]. Asterisked symbols represent data which have been obtained by extrapolation from lower temperatures.

NMR and still being observable by uptake measurements,[3] an especially large number of investigations were concentrated on benzene in zeolite NaX. For this system, uptake measurements by different research groups revealed both agreement[11] and disagreement[10,12] with the NMR data. Being aware of the fact that uptake and NMR measurements refer to different physical situations,[10] namely to non-equilibrium and equilibrium conditions, respectively, in the present study quasi-elastic neutron scattering[13] has been applied as an independent method for the observation of translational molecular motion under equilibrium conditions.

The neutron scattering experiments have been carried out at the Institut Laue-Langevin, Grenoble, using the time-of-flight spectrometer IN5 with an incident wavelength of 0.9 nm (corresponding to 1.0 meV) and an elastic resolution of *ca.* 19 μeV. Following the procedure described in refs. 13 and 14, information about translational molecular motion has been determined by analysis of the broadening, as a function of the neutron momentum transfer, of the energy distribution of the neutrons scattered incoherently by the hydrogen atoms of benzene. It was found that the translational motion of benzene could be described by the jump diffusion model of Singwi and Sjölander,[15] assuming that the molecule spends more time in its oscillary state than diffusing. A more detailed description of the results, including the rotational motion, will be reported elsewhere.[16] The measurements were carried out with commercially available zeolite NaX (Union Carbide Corporation).

Table 1 gives a summary of the self-diffusion coefficients determined and mean jump lengths $<l^2>^{1/2}$ at 458 K at three different sorbate concentrations. In Figure 1, these diffusivities are included in a comparison of the results of previous NMR pulsed field-gradient measurements with the results of non-equilibrium (*i.e.*, adsorption/desorption) experiments. The diffusion coefficients, D_d, obtained in the non-equilibrium measurements have been transferred into the so-called corrected diffusivities D_o by applying equation (1), where $c(p)$

$$D_o = D_d \frac{\mathrm{d}\ln c(p)}{\mathrm{d}\ln p} \qquad (1)$$

denotes the sorbate concentration in equilibrium with a sorbate atmosphere of pressure p. In many cases (and, in particular, for sufficiently small sorbate concentrations) D_o may be shown to coincide with the self-diffusion coefficient.[10] It appears from Figure 1 that in both the absolute values and the trends in the concentration dependence, the neutron scattering data confirm the validity of the NMR results. There should not be any question, therefore, that the intracrystalline mobility of benzene in zeolite NaX is correctly represented by the NMR and neutron scattering self-diffusion data (open symbols in Figure 1). Remaining differences may be attributed

Table 1. Diffusion data for benzene in zeolite NaX at 458 K as obtained by quasi-elastic neutron scattering.

Sorbate concentration, c/molecules per supercage	$<l^2>^{1/2}/$ nm	$D/$ $10^{-10}\,m^2\,s^{-1}$
0.8	0.46	7
1.3	0.35	4
2	0.24	1.9

to differences in the sample origin and/or sample preparation, as well as to the uncertainty of the measurements (which may amount to a factor of two). The corrected diffusivities reported in ref. 11 are of this order of magnitude. The reason why other well-documented adsorption/desorption studies (lower experimental points of Figure 1) lead to different results, is not yet clear.

The decrease in the mean jump lengths with increasing sorbate concentration (*cf.* Table 1) is in agreement with the result of previous NMR diffusion and relaxation studies of hydrocarbons in NaX, where the decrease in the translational mobilities could be shown to be mainly due to a reduction of the mean jump lengths rather than to increasing mean residence times between succeeding jumps.[19]

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References

1 H. Pfeifer, 'NMR Basic Principles and Progress,' Springer-Verlag, Berlin, 1972, vol. 7.
2 J. Kärger and J. Caro, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1363.
3 R. M. Barrer, 'Zeolites and Clay Minerals as Adsorbents and Catalysts,' Academic Press, London, 1978.
4 M. Bülow and G. Öhlmann, and reply by D. M. Ruthven, in 'Discussion of the 7th International Conference on Zeolites,' ed. H. Tominaga, Japan Association of Zeolites, 1986, p. 67.
5 H.-J. Doelle and L. Riekert, *ACS Symp. Ser.*, 1977, **40**, 401.
6 L.-K. Lee and D. M. Ruthven, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 2406.
7 M. Bülow, J. Kärger, M. Kočiřik, and A. M. Voloshchuk, *Z. Chem.*, 1981, **21**, 175.
8 J. Kärger and D. M. Ruthven, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1485.
9 N. G. Van-Den-Begin and L. V. C. Rees, in 'Zeolites: Facts, Figures, Future,' eds. P. A. Jacobs and R. A. Van Santen, Elsevier, Amsterdam, 1989, p. 915.
10 J. Kärger and D. M. Ruthven, *Zeolites*, 1989, **9**, 267.
11 M. Bülow, W. Meith, P. Struve, and P. Lorenz, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 2457.
12 M. Eic, N. V. Goddard, and D. M. Ruthven, *Zeolites*, 1988, **8**, 327.
13 H. Jobic, A. Renouprez, M. Bée, and C. Poinsignon, *J. Phys. Chem.*, 1986, **90**, 1059.
14 H. Jobic, M. Bée, J. Caro, M. Bülow, and J. Kärger, *J. Chem. Soc., Faraday Trans. 1*, 1989, **12**, 4201.
15 K. S. Singwi and A. Sjölander, *Phys. Rev.*, 1960, **119**, 863.
16 H. Jobic, M. Bée, and G. J. Kearley, in preparation.
17 A. Germanus, J. Kärger, H. Pfeifer, N. N. Samulevich, and S. P. Zhdanov, *Zeolites*, 1985, **5**, 91.
18 P. Lorenz, M. Bülow, and J. Kärger, *Izv. Akad. Nauk USSR, Ser. Khim.*, 1980, 1741.
19 J. Kärger, H. Pfeifer, M. Rauscher, and A. Walter, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 717.