Adsorption 7: 301–304, 2001

Short Communication: Diffusion of Simple Molecules in 4A Zeolite

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Received April 24, 2001; Revised August 2, 2001; Accepted August 2, 2001

Abstract. Recently reported diffusivity data for N_2, CH_4 and Kr in 4A zeolite pelleted adsorbent are compared with earlier data for the same sorbates in several different 4A samples. It is shown that, although there are large differences in diffusivity between the different adsorbent samples the activation energies are essentially constant. The data can be reconciled if it is assumed that the samples contain different fractions of "open" windows as a result of non-ideal distribution of the Na^+ cations.

Keywords: diffusion, 4A zeolite, N_2, Kr, CH_4

In a recent paper Cao et al. (2000) reported self-diffusivities for N_2, CH_4 and Kr in a sample of commercial 4A zeolite adsorbent. These same systems have been the subject of several previous experimental studies since the pioneering work of Habgood in 1958 (Ruthven and Derrah, 1975; Yucel and Ruthven, 1975; Kondis and Dranoff, 1971; Kumar and Ruthven, 1979; Eagan and Anderson, 1975; Doetsch, 1975; van de Voorde et al., 1990; Habgood, 1958; Alloneau and Volino, 1986). A comparison of the recent data with the earlier results provides useful insight into their behavior.

Selected diffusivity data are summarized in Fig. 1. In choosing these data for consideration we have retained only the measurements which extend over a sufficiently wide range of temperature to allow reliable determination of the activation energy and for which the zeolite crystals were large enough to ensure that sorption rates were not significantly affected by thermal effects or extracrystalline resistance to mass transfer. For example, the data of Habgood (1958), which were obtained with sub-micron sized commercial crystals, have not been included. Since, at low sorbate concentrations (within the Henry's Law region), the self and transport diffusivities should coincide, direct comparison of the recent limiting self-diffusivities with earlier values of the limiting transport diffusivity is valid. It is evident that even though all samples are nominally designated as 4A (NaA) there are substantial differences in diffusivity although the diffusional activation energy is essentially constant. The data of Kumar and Ruthven (1979) and van de Voorde et al. (1990) both of which refer to Linde 4A pelleted material, fall essentially on the same line.

It has long been recognized that diffusion in commercial zeolite adsorbents occurs more slowly than in large ideal zeolite crystals and this difference has been shown to be related to the severity of the conditions used in dehydration/pelletization of the industrial adsorbents (Kondis and Dranoff, 1971). It has been suggested that partial collapse of the zeolite structure at the surface, under severe hydrothermal conditions, may lead to a surface barrier which increases the overall mass transfer resistance. However, although such an effect has been demonstrated (Bülow et al., 1982; Kärger et al., 1982) it cannot explain the present data. The results of Cao et al. (2000) show clear conformity with a diffusion model (uptake proportional to $\sqrt{time}$ in the initial region) rather than with a surface resistance model (initial uptake directly proportional to time). The earlier data also conform to a diffusion model and Yucel confirmed this by carrying out the measurements with different crystal sizes (Yucel and Ruthven, 1975). The time constant was found to vary with the *square* of the equivalent crystal radius, as required for diffusion control.

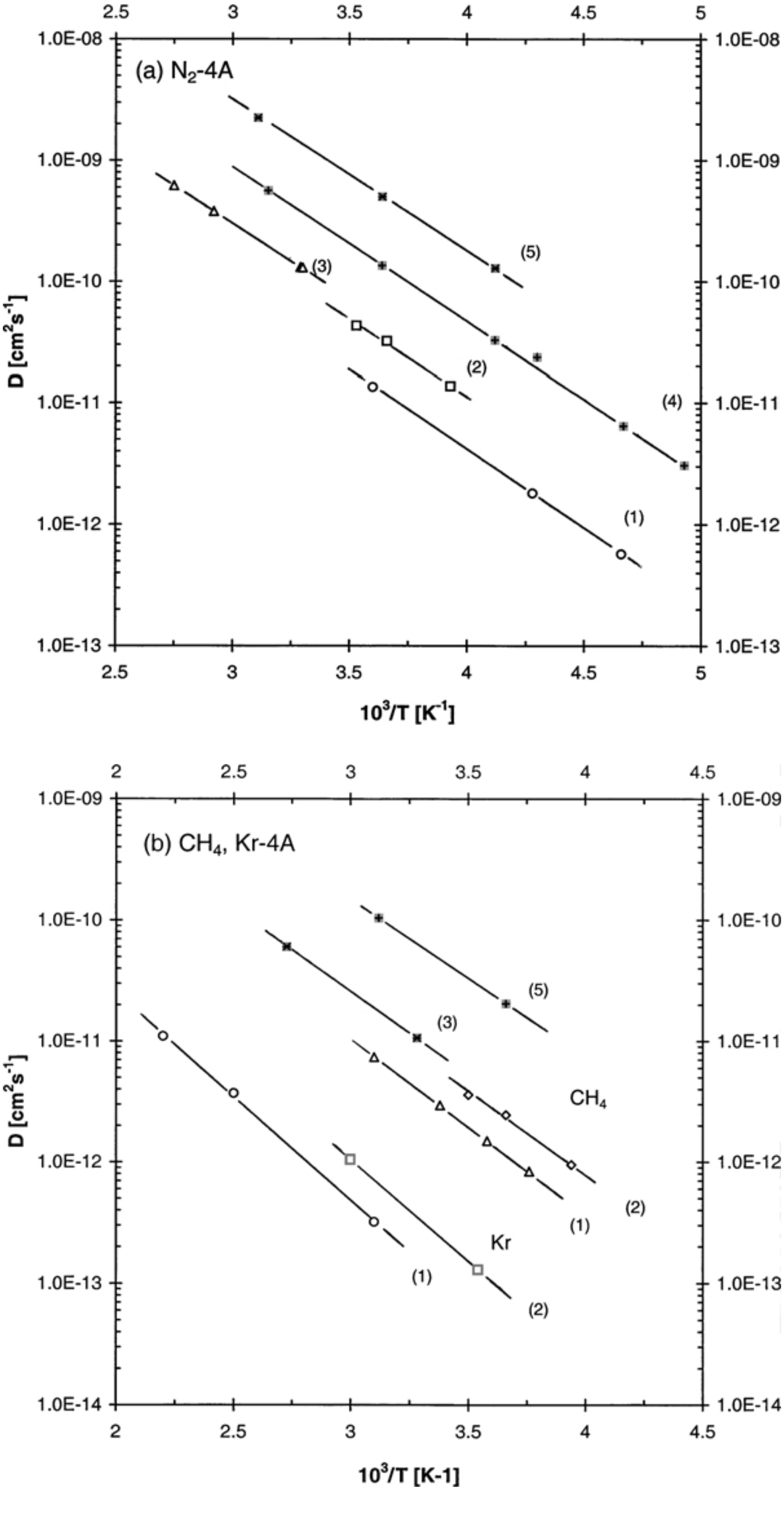

Figure 1. Arrhenius plots showing temperature dependence of diffusivity (a) N_2-4A; (b) CH_4-4A and Kr-4A. The numbers on the lines refer to the different samples as noted in Table 1.

The constancy of the activation energy suggests that the samples differ in the average distance traveled between barriers, rather than in the height of the diffusion barriers. The most obvious explanation relates to the cation distribution. It is generally assumed that, in the 4A zeolite, all the 8-ring windows are partially obstructed by the presence of an Na^+ cation (Breck, 1974). However, if some of the windows are unobstructed (because the Na^+ cations are located in the energetically less favorable site III rather than site II) the diffusivity will increase dramatically with little or no change in the activation energy (Ruthven, 1974). In conformity with this hypothesis the diffusivity ratios for several different sorbates in different 4A zeolite adsorbent samples are seen to be very similar.

In order to obtain a more quantitative interpretation of these data we make the assumption that the 4A sample that shows the lowest diffusivity (Linde 4A crystals lot 470017, studied by Ruthven and Derrah (1975) and Doetsch (1975) represents the ideal 4A with all windows obstructed by an Na^+ cation. The diffusivity in this sample is designated as D_*. Since, for the sorbates under consideration (N_2, CH_4 and Kr), the ratio of the diffusivities in the "open" (CaA) and "closed" (NaA) forms is high, one can easily estimate the fraction of unobstructed windows from the ratio D/D_*, using the limiting curve for the random walk model (Fig. 2 of Ruthven (1974)).

The results of such an analysis are summarized in Table 1. Taken together all the data are reasonably consistent and suggest that the fraction of "open" windows in these 4A samples varies from about 0.23 for the sample studied by Cao to about 0.33 for the Yucel samples. These differences correspond to a variation in the diffusivity by more than an order of magnitude and are clearly critical when making comparisons between the data reported by different researchers.

According to this model the values of x determined, for a given adsorbent, from the diffusivity data for different sorbates, should be the same. The values are indeed similar with the exception of sample 3 which shows a significant difference between CH_4 and N_2 (0.17/0.24). However, small differences

Table 1. Summary and analysis of diffusivity data.

Sorbate	Sorbent	Ref.	*T* range (K)	*E* (kcal/mole)	Ratio (Av) D/D_*	x
N_2	(1) Linde 4A crystals (3.2 μm) Lot 470017	Ruthven and Derrah (1975)	215–277	6.1	1.0	0
	(2) UOP 4A pellet (crystals 1.95 μm)	Cao et al. (2000)	253–283	5.3	2.54	0.23
	(3) Linde 4A pellet	Kumar and Ruthven (1979)	304–336	6.0	3.5	0.24
		van de Voorde et al. (1990)	303–343	5.3	3.4	0.24
	(4) Linde 4A crystals	Eagan and Anderson (1975)	195–233	5.8	9.6	0.29
	4.1 μm Lot 450339	Ruthven and Derrah (1975)	243–325			
	(5) Lab synthesized 4A crystals (7.1, 22, 34 μm)	Yucel and Ruthven (1975)	243–323	5.6	35	0.33
CH_4	(1) Linde 4A crystals (3.2 μm) Lot 470017	Doetsch (1975)	323–389	6.0	1.0	0
	(2) UOP 4A Pellet (crystals 1.95 μm)	Cao et al. (2000)	253–283	6.4	2.5	0.23
	(3) Linde 4A pellet	Kumar and Ruthven (1979)	305–366	6.4	1.3	0.17
	(4) Lab synthesized 4A crystals (7.1, 22, 34 μm)	Yucel and Ruthven (1975)	273–323	5.9	20	0.31
Kr	(1) Linde 4A crystals (3.2 μm) Lot 470017	Derrah and Ruthven (1975)	323–473	8.1	1.0	0
	(2) UOP 4A Pellet (crystal 1.95 μm)	Cao et al. (2000)	283–333	7.7	2.3	0.22

x = Fraction of "open" windows.

in the regeneration procedure can affect the cation distribution so such a difference between different sets of experiments is probably not surprising. Although the actual situations may well be more complicated than is contemplated here it appears that the simple model in which the differences between the samples studied by different investigators is attributed to differences in the distribution of Na^+ cations between the window and framework sites is capable of explaining the main features of the diffusional behavior.

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