Measurement of Xenon Distribution Statistics in Na-A Zeolite Cavities

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^{129}Xe NMR spectroscopy has been used to probe directly the distribution of xenon atoms confined in atomic-size Na-A zeolite cavities. For mean xenon occupancies less than about three Xe atoms per α-cage, the guest populations are well described by binomial statistics. At higher guest loadings the finite volumes of the xenon atoms become significant, as reflected by a fit of the experimental populations with a hypergeometric distribution, with a maximum of seven Xe atoms per cage. At the highest xenon loadings the experimental distribution is narrower than hypergeometric, as predicted by Monte Carlo simulations.

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Recently, there has been a great deal of interest in probability functions that describe the distribution of atoms and molecules over small independent subvolumes.[1-5] These modeling efforts have advanced significantly the theoretical basis for phenomena associated with transitions between phases, adsorption in small pore spaces, and configurations of molecules in bulk gases and liquids. Though the importance of local dynamics and structure to a fluid system's macroscopic behavior is well known,[6-8] correlations with developing molecular theories and numerical simulations have proven difficult because there are few experimental data. We report in this Letter the experimental measurement of distribution probabilities for atoms confined in small, independent subvolumes, specifically for high-pressure xenon occluded in microporous Na-A zeolite cavities.

Na-A zeolite provides an ordered matrix that can trap clusters of atoms and molecules in its void space if the molecular diameter of the guest slightly exceeds the pore diameter of the zeolite at room temperature. Assemblies of 0.44-nm-diam xenon atoms, for example, can be introduced into the α-cages of Na-A zeolite through framework windows 0.42 nm in diameter at room temperature, by heating the zeolite to 523 K in the presence of xenon gas. Subsequent cooling of the Xe-Na-A system to room temperature results in the confinement of xenon guest species inside the 1.14-nm-diam Na-A α-cages, as illustrated schematically in Fig. 1. The ^{129}Xe chemical shift is sensitive to local interactions experienced by adsorbed xenon atoms and has been used to distinguish different populations of xenon in Na-A cavities,[9,10] as well as distributions of other guest molecules.[11] The distribution of occluded xenon guests within the Na-A α-cages can be modified by varying the equilibrium xenon loading pressure at 523 K.

Na-A zeolite samples were dehydrated by heating at 673 K under vacuum (less than 10^{-5} torr) for 10 h in a 1-cm-diam stainless-steel, high-pressure bomb. After cooling the zeolite to room temperature, approximately 1-3 mmol xenon (a natural-abundance mixture of isotopes, including ^{129}Xe and ^{131}Xe) was introduced to the bomb at 298 K using a standard vacuum rack apparatus. High xenon loading pressures were produced by first condensing the gas in the bomb assembly (immersed in a liquid-nitrogen bath), isolating the bomb from the vacuum rack, and then reexpanding the xenon gas into the 10-cm^3 bomb volume. The zeolite samples in the bomb were heated to 523 K for 4 h (8 h for the sample loaded at 210 atm), permitting xenon atoms to penetrate the expanded Na-A α-cage network. Xenon loading pressures of up to 210 atm at 523 K were achieved under conditions of adsorption equilibrium. The samples were subsequently quenched by immersion of the bomb in an ice-water bath, trapping the xenon atoms in the Na-A α-cages. Quenching rates were varied from about 0.02 to 2 K/s with no detectable effect on the xenon distribution in samples otherwise treated identically. Similarly, no changes in xenon distribution were observed in samples heated for longer periods of time.

After quenching, the Xe-Na-A samples were transferred to glass ampoules in a glove box under dry nitrogen to prevent contamination by atmospheric moisture. The sample-containing ampoules were then evacuated,

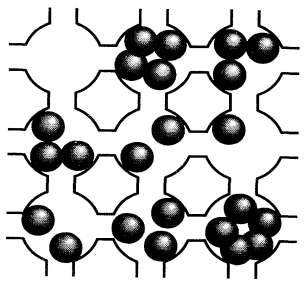

FIG. 1. Schematic diagram of xenon atoms distributed within the α-cages of Na-A zeolite.

charged with 100 torr of dry oxygen gas, and finally sealed. The addition of a small quantity of paramagnetic oxygen reduced the spin-lattice relaxation time (T_1) of ^{129}Xe in these samples, allowing use of shorter delays (typical 1 s) between 90° pulses. Xenon-129 NMR spectra were obtained after signal averaging 5000–10000 scans on a spectrometer operating at 110 MHz. Chemical shifts are referenced to xenon gas at very low pressure[12] and are accurate to ± 0.5 ppm.

Figure 2 shows room-temperature ^{129}Xe NMR spectra of dehydrated Na-A zeolite samples containing occluded xenon atoms adsorbed under different equilibrium loading pressures at 523 K. The ^{129}Xe nuclei become less shielded with increasing guest density,[13] so that multiple peaks are observed from a single Xe–Na-A sample. Xenon atoms in Na-A α-cages with different guest occupancies have characteristic NMR frequencies that permit the relative populations of α-cages containing different numbers of xenon guests to be determined. Each peak corresponds to a ^{129}Xe signal from α-cages containing a different number of occluded xenon atoms. Small variations in the chemical shift of ^{129}Xe in cavities containing identical xenon populations are most likely

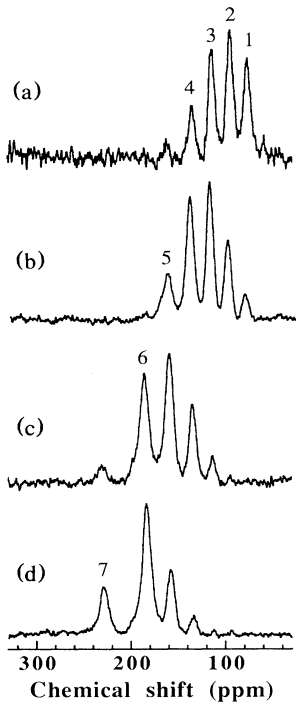

FIG. 2. Room-temperature ^{129}Xe NMR spectra of xenon occluded in Na-A zeolite at 523 K at different equilibrium loading pressures: (a) 8 atm, (b) 40 atm, (c) 150 atm, and (d) 210 atm. Each peak corresponds to a ^{129}Xe signal from xenon in α-cages containing different numbers of occluded Xe atoms (indicated by the numbers above the respective peaks). The chemical shifts are referenced to xenon gas at very low pressure.

due to small amounts of coadsorbed water. The distribution of xenon in these different cage environments can be determined from the relative areas of the peaks in the ^{129}Xe NMR spectrum. As illustrated in Fig. 2, xenon occupancy of the Na-A α-cages is a sensitive function of the xenon loading pressure at equilibrium. The data show a monotonic increase in the mean xenon population $\bar{n}$ as the loading pressure is increased, with xenon occupancy of the α-cages approaching an apparent loading limit of about seven Xe atoms/α-cage.

At low xenon loadings, where the atomic volume of the xenon is negligible, the distribution of atoms should be well described by binomial statistics. For a loading of N_0 xenon atoms in an ensemble volume V_0, the probability of finding an α-cage with n xenon guests can be represented by a binomial distribution:

$$f_{N_0,p}(n) = \binom{N_0}{n} p^n (1-p)^{N_0-n}, \tag{1}$$

where $f_{N_0,p}(n)$ is the normalized number of Na-A α-cages in an ensemble volume V_0 possessing n xenon guests, and $p = V/V_0 = \bar{n}/N_0$ is the probability that a xenon atom will occupy a given α-cage with subvolume V. As observed by Rowlinson and Woods,[4] the probability p is not constant, but varies as a weak function of xenon occupancy according to the degree of subvolume independence. The xenon populations $f(n)$ are measured experimentally for xenon atoms occluded in Na-A α-cages (for $n > 0$) by integrating the peaks in the ^{129}Xe NMR spectra of Fig. 2.

As illustrated in Fig. 3(a) for Xe–Na-A systems with mean populations $\bar{n}$ of less than about three Xe atoms/α-cage, agreement is excellent between the experimentally measured xenon occupancies $f(n)$ and those values predicted by binomial statistics. As the loading pressure is increased, the finite sizes of the guest atoms play an important role in establishing the xenon occupancies observed in Figs. 3(b)–3(d). Güémez and Velasco[1] have suggested that the distribution of atoms with finite volumes (or equivalently, among mutually exclusive lattice sites) should display a hypergeometric dependence of the form[14]

$$f_{N_0,p}(n) = \binom{N_0}{n}\binom{M-N_0}{K-n} \Big/ \binom{M}{K}, \tag{2}$$

where $M = V_0/\sigma$ is the total number of lattice sites available in the ensemble volume V_0, $K = V/\sigma = pM$ is the number of lattice sites available in a single α-cage with subvolume V, σ is an effective atomic volume of the xenon guests, and $N_0 = \bar{n}/p$ is the ensemble xenon population as before. After substituting for M and N_0, Eq. (2) becomes

$$f_{N_0,p}(n) = \binom{\bar{n}/p}{n}\binom{K/p-\bar{n}/p}{K-n} \Big/ \binom{K/p}{K}, \tag{3}$$

with $\bar{n}$ and K representing adjustable parameters.

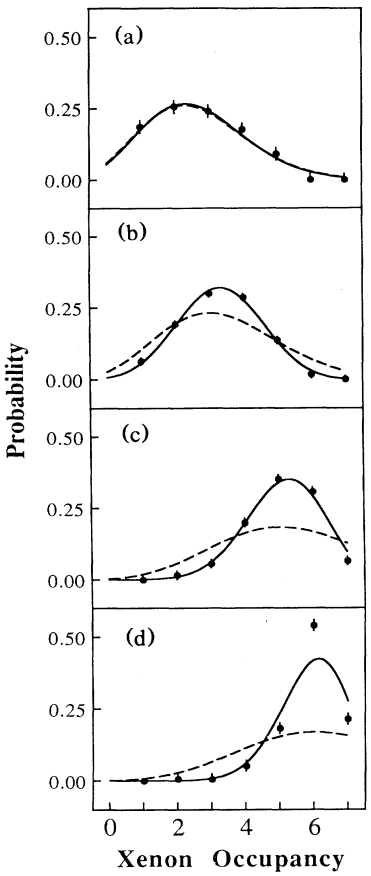

FIG. 3. Plots of normalized experimental ^{129}Xe NMR peak areas, $f(n)$, (solid circles) vs the number of xenon atoms occluded in Na-A α-cages at different loading pressures (the mean number of xenon atoms per cavity, $\bar{n}$, is also provided for each sample): (a) 8 atm, $\bar{n} \approx 2.5$; (b) 40 atm, $\bar{n} \approx 3.4$; (c) 150 atm, $\bar{n} \approx 5.1$; and (d) 210 atm, $\bar{n} \approx 5.9$. Accompanying the data are binomial (dashed line) and hypergeometric (solid line) best fits to the data computed using Eqs. (1) and (3). A probability of $p = \frac{1}{8}$ provided best fits to the data over the range of xenon occupancies investigated, and this value was used for all of the fits shown. The data in (a) have been normalized using the $f_{N_0,p}(0)$ value of the binomial distribution to estimate the fraction of empty α-cages.

As shown in Fig. 3(a), for low xenon loadings ($\bar{n} < 3$ Xe/α-cage), the binomial and hypergeometric fits to the ^{129}Xe NMR data are nearly coincident. For mean xenon populations $\bar{n}$ above about 3 Xe/α-cage [Figs. 3(b) and 3(c)], the hypergeometric fits obtained using Eq. (3) with $K = 7$ agree well with the ^{129}Xe NMR data, consistent with the maximum number of xenon atoms observed in the spectrum of Fig. 2(d). The effective (excluded) volume of xenon σ, computed to be approximately 110 Å^3, is larger than the 45 Å^3 associated with the volume of a single xenon atom, an indication of inefficient packing of xenon guests in the confined α-cage environments. In all cases examined, agreement is excellent between the average xenon occupancies derived from the hypergeometric fits and those determined experimentally from integration of the peaks in the spectrum of Fig. 2.

At the highest xenon loading studied here ($\bar{n} = 5.9$), the observed xenon distributions are consistently narrower than the binomial and hypergeometric predictions [Fig. 3(d)]. This may arise from nonequilibrium conditions produced by hindered diffusion of xenon atoms through Na-A cavities crowded with other xenon guests. However, a narrow probability distribution is also the result anticipated (from Monte Carlo simulations, for example) for real fluids, with continuously moving molecules, that present a less-accommodating configuration for placement of a molecular guest in an arbitrary subvolume.[4] Moreover, the geometric constraints imposed by the α-cages on guest packing configurations are undoubtedly appreciable, especially at high guest loadings. Separate theoretical studies[15–17] and adsorption experiments[18,19] indicate that xenon atoms have a strong affinity for aluminosilicate surfaces and consequently maintain close proximity to the α-cage walls as a highly mobile, adsorbed phase at room temperature. The result is that xenon packing arrangements are almost certainly dominated by local surface effects and geometric constraints even at low guest loadings. Based on an idealized geometric model, a pentagonal bipyramidal arrangement of xenon atoms tangent to the interior walls of the α-cages appears feasible near the saturation occupancy when $n = 7$ Xe atoms per cavity. Recent Monte Carlo simulations have indeed demonstrated the likelihood of such xenon polyhedra in Na-A:[20] Assemblies of six xenon atoms are expected to possess cubic symmetry, while a lower symmetry configuration is anticipated when $n = 7$. Theoretical prediction of the maximum number of xenon guests capable of being accommodated inside a Na-A α-cage remains an open and challenging problem.

To conclude, our experimental results provide atomic distribution statistics for different guest loadings in a macroscopic ensemble. These data clearly demonstrate the role of finite atomic volume on occupancies in small subvolumes, indicating that atoms in the cavities of the zeolite behave as subvolumes of a finite fluid and not as subvolumes in independent equilibrium with an infinite reservoir. Local structural information provided by microscopic distribution probabilities has important consequences for the prediction of bulk and confinement-modified fluid properties, particularly as they relate to transitions between phases or to adsorption and transport in microporous materials.

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