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Here M = Mo but other results[6] are indicative of a similar behavior with oxotungstate supported on alumina. However, there exist some differences between these two systems. The transformation oxysulfide → sulfido compounds seems rather difficult when M is the tungsten.

The MoS_2 final product has been characterized by both HREM and LRS. A correlation exists to indicate that the Raman lines characteristic of MoS_2 are sensitive to their crystal size. Dehydration of a sample before sulfidation noticeably affects the size of the supported MoS_2 slabs.

Registry No. Mo, 7439-98-7; H_2S, 7783-06-4; MoS_2, 1317-33-5.

Molecular Motion of Benzene, *n*-Hexane, and Cyclohexane in Potassium Zeolite L Studied by Deuterium NMR

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The molecular motions of perdeuterated benzene, *n*-hexane, and cyclohexane sorbed at loading levels of 1 molecule per channel lobe (or, equivalently, per unit cell) in potassium zeolite L have been examined by ^2H nuclear magnetic resonance (NMR) for 100 K $\leq T \leq$ 350 K. Benzene (C_6D_6) gives a broad signal with, for $T < \sim 150$ K, a quadrupolar splitting of half of the static value, interpreted in terms of rapid reorientation in the molecular plane. This mode of motion is consistent with the location of benzene in capping positions above channel wall site potassium cations observed at 78 K by powder neutron diffraction. For temperatures above ~250 K, a less broad component (interpreted as indicating activated benzene site hopping) develops. Sorbed *n*-hexane (C_6D_{14}) also shows no evidence for isotropic motion. Two distinct spectral components, associated respectively with the methyl and methylene deuterons, are observed. The magnitudes of the ^2H quadrupolar coupling strengths can be interpreted solely in terms of torsional rotations about the carbon–carbon bonds. The temperature dependence of the ^2H spin–lattice relaxation processes suggests an activation energy of ~2 kcal mol^{-1} for these C–C bond rotations, consistent with earlier studies of bond rotation in alkanes. Sorbed cyclohexane (C_6D_{12}) shows a transition in the dynamical behavior (on the time scale of the ^2H NMR experiment) in the vicinity of 280 K. Close to 280 K, a narrow signal is observed consistent with effectively isotropic reorientations, but both above and below 280 K there is a significant residual quadrupole interaction. The narrow component decreases rapidly with temperature, becoming unobservable below 230 K.

Introduction

The mobilities of hydrocarbons sorbed within zeolites can be probed by several techniques.[1] Such measurements can generally yield intracrystalline diffusion coefficients but provide little information about the character of the hydrocarbon motion on a molecular level. In deuterium (^2H) NMR experiments, molecular motions that are faster than the time scale of the NMR measurement (~10^{-6} s) lead to reductions in the effective quadrupolar coupling constants.[2] Analysis of these effects provides information about the nature of the molecular motion. Measurements on aromatic hydrocarbons in zeolite ZSM-5,[3-7] on benzene in zeolite X,[5,7,8] and on dimethyl ether,[9] NH_4^+ groups,[10] water and methanol,[11] and methylamines[12] in zeolite rho have already demonstrated the applicability of these types of measurement to the study of sorbed phases within zeolites. Measurements on similar species in other constrained environments have also been reported.[13-16]

In the present paper, we describe ^2H NMR experiments on three perdeuterated C_6 hydrocarbons, benzene, *n*-hexane, and cyclohexane, sorbed at loading levels of 1 molecule per channel lobe (or, equivalently, per unit cell) within potassium zeolite L. These molecules differ significantly in their shapes and internal degrees of freedom and give rise to very different types of motion when sorbed within the zeolite L host.

Deuterium NMR Properties

The resonance properties of the ^2H nucleus are dominated by the interaction of the ^2H nuclear quadrupolar moment with the electric field gradients in its vicinity. These electric field inhomogeneities at the site of a ^2H nucleus in a ···C–D bond arise from the positive charge of the neighboring carbon nucleus and the negative charge of the electrons in the bond itself.[2] In the NMR experiment, the three spin states of the $I = 1$ ^2H nucleus are split by the static magnetic field,[17] and the quadrupole interaction causes an additional shift of these spin energy states (which reflects the angular dependence given in eq 1 below). For a powder sample in which individual grains have an arbitrary orientation with respect to the applied magnetic field, the weighted average of the orientations yields a characteristic "horned" spectrum (see, e.g., Figure 1). Improved abilities to calculate the electronic properties of molecules enable the quadrupolar interaction strengths to be calculated to an accuracy of ~2%.[18] In addition, quadrupolar

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interactions have been measured by NMR techniques for a variety of organic and inoganic molecular species, with accuracies approaching ~1%,[19] providing reference points that permit interpretations of effective quadrupolar interactions in other systems.

The full static quadrupole interaction of deuterium in organic compounds produces splittings and line broadenings of ~200 kHz, but molecular motion can lead to an averaging and consequent reduction from the effective static magnitude. The quadrupole interaction Hamiltonian can (assuming an axial field gradient) be written as[20]

$$H = (e^2qQ/h)_0\{3/\cos^2\Theta - 1\}\{3I_z^2 - I(I+1)\} \quad (1)$$

where eq is the strength of the electric field gradient, eQ is the magnitude of the ^2H nuclear quadrupolar moment, and Θ is the angle between the principal axis of the electric field gradient and the applied magnetic field. If the molecule moves on a time scale fast compared to the strength of this interaction (that is, with a correlation time τ of $\tau < (e^2qQ/h)_0^{-1}$) the motion will lead to an averaging of this interaction. For completely isotropic motion the interaction vanishes because the spherical average of $\{3\cos^2\Theta - 1\}$ is zero. If the motion is only partial, spinning about a particular axis, for example, the interaction may also be only partially reduced. By the addition theorem of spherical harmonics, it can be demonstrated that, for rotation about one axis, oriented at an angle β with respect to the direction of the electric field gradient[21]

$$\{3\cos^2\Theta - 1\} = ([3\cos^2\beta - 1]/2)(3\cos^2\Theta' - 1) \quad (2)$$

where Θ' is the angle between the axis of rotation and the magnetic field. The term $[3\cos^2\beta - 1]/2$ is the reduction factor of the quadrupole interaction strength associated with this motion. If the molecular motion consists of several such rotations, the product of the individual reduction factors is taken to determine the final interaction strength. Torsional motions and vibrations can also reduce the quadrupolar interaction strength. The reductions in the strength of the quadrupole interactions are reflected in a reduced splitting between the "horns" of the powder spectrum.

Inferences based on the shape of the spectrum are most straightforward when the rates of molecular motion are significantly greater or less than (e^2qQ/h). When the rates approach (e^2qQ/h), interpretation (although still practicable[22]) becomes more complex. Information about the absolute magnitude of these rates is contained in the spin–lattice relaxation characteristics of the ^2H nuclei. On perturbing the thermal equilibrium population of the nuclei by applying rf pulses, these spin–lattice relaxation processes will restore the equilibrium conditions at a rate $(1/T_1)$, which, for fluctuations of the quadrupolar coupling $\Delta[e^2qQ/h]$, will have the form[23]

$$1/T_1 = [3\pi^2/4]\{\Delta[e^2qQ/h]\}^2[J(\omega_0) + 4J(2\omega_0)] \quad (3)$$

where $J(\omega) = 2\tau_c/(1 + \omega^2\tau_c^2)$, τ_c is the correlation time for the molecular motion, and ω_0 is the Larmor frequency of the ^2H nuclei. For isotropic motions describable with a single correlation time, all of the quantities are known and we can determine τ_c. For the present materials, measurements of the T_1 values were made as a function of temperature from 293 to 140 K. Activation energies for the molecular motions responsible for the relaxation were then deduced from plots of the logarithm of $1/T_1$ as a function of $1/T$ (see, e.g., Figures 4 and 8 below).

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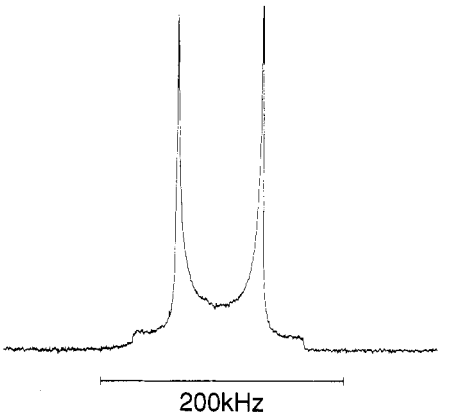

Figure 1. Fourier transform of the ^2H nuclear free induction decay for C_6D_6 in zeolite L at 150 K at a loading of 1 molecule per unit cell.

Experimental Section

Chemical analysis of the typical sample of potassium zeolite L used here as substrate (by inductively coupled plasma emission spectroscopy, ICPES) gave the formula $Na_{0.03}K_{9.27}Al_{9.30}Si_{26.70}O_{72}\cdot nH_2O$. This material has also been characterized by ^{29}Si NMR, thermogravimetric analysis, *n*-hexane sorption, and powder X-ray diffraction. The complete structure of the dehydrated zeolite has been determined by neutron powder diffraction.[24]

Several series of samples were prepared. In a typical preparation, zeolite L was dehydrated by heating gradually over several hours in air to ~770 K and held at that temperature overnight. The hot powder was allowed to cool in a desiccator. Samples (~1.5 g) were transferred in a N_2-flushed glovebag to tared vials that were crimp-sealed with aluminum-faced silicone rubber septa. Appropriate volumes of the perdeuterated hydrocarbons were injected into the vials via syringe (all KOR isotope service, nominally C_6D_6 99.96% D, C_6D_{14} 98% D, C_6D_{12} 99.5% D). Loading levels were determined gravimetrically by uptake and for the three samples discussed in detail here correspond to 0.96 (C_6D_6), 1.08 (C_6D_{14}), and 0.97 (C_6D_{12}) molecules per unit cell. To ensure a homogeneous distribution of hydrocarbon throughout the samples, the tubes were alternately agitated in a mechanical tumbler and heated to ~370 K. Finally they were left at 373 K overnight. Samples thus homogenized were transferred to NMR tubes in a N_2-flushed glovebag. The septum was punctured with a cork borer and the thin neck of the glass tube inserted to form a tight seal. The assembly could then be removed from the bag, inverted, and vibrated gently to form a closely packed bed. The filled NMR tube was rapidly attached to a vacuum line, cooled in liquid nitrogen, and evacuated just enough to permit sealing with a torch. Variations of this procedure that gave essentially identical results involved dehydration of the zeolite under vacuum, restricting the homogenization step to mechanical tumbling at 298 K, and loading the NMR tubes directly under dry N_2. Proton NMR measurements on the same sealed samples indicated that adventitious water contents in the samples thus prepared were low.

The NMR observations were generally made with a Bruker MSL NMR spectrometer system operating at ~55.3 MHz. The magnetic field for the measurements was provided by an Oxford Superconducting Solenoid system operating at a field of ~85 kG. The data collected were the free induction decay signals of the ^2H nuclei. These decays were then Fourier transformed to obtain the absorption spectrum.

Results and Discussion

Benzene. A typical signal for C_6D_6 in potassium zeolite L at $T < \sim 200$ K is shown in Figure 1. The free induction decay response of the ^2H nuclear magnetization shows a characteristic beat patern which transforms into the "horned" absorption spectrum. For a nucleus of $I = 1$, the effective static quadrupole

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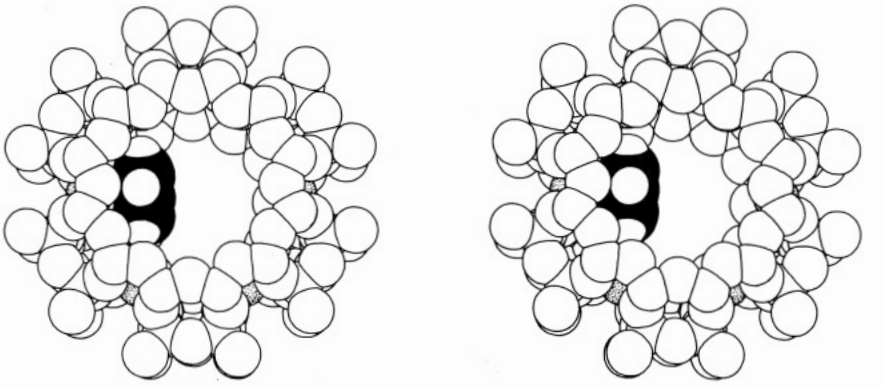

Figure 2. Cross-stereoview of the capping site for benzene above a channel wall potassium cation in zeolite L as determined by powder neutron diffraction[25] (Si/Al,O,H, open circles; C, solid; K, speckled). Only one of six equivalent locations is drawn.

coupling is related to the splitting between these principal components, ΔH_Q, by[26]

$$(e^2qQ/h)_{eff} = (4\gamma/3)\Delta H_Q \quad (4)$$

where γ is the nuclear gyromagnetic factor. The observed splitting of 106.7 G in magnetic field units translates into an effective value $(e^2qQ/h)_{eff} = 93.0$ kHz, which indicates that the molecules are spinning in their molecular plane, i.e., about the 6-fold molecular symmetry axis. The static value of the quadrupole interaction for C_6D_6 is 183 ± 10 kHz,[27] and for such motion, the axis of spinning is perpendicular to the principal directions of the electric field gradients at the ^2H nuclei. From eq 2, if the angle between the gradient direction and the reorientation axis is $\beta = 90°$, the reduction factor $[3\cos^2\beta - 1]/2$ is equal to $-1/2$, exactly as observed here. The agreement between observed and calculated values implies that for $T < \sim 150$ K other effects such as torsional motions or rocking do not contribute significantly to the averaging process.

This mode of motion of the benzene molecules is consistent with the behavior anticipated on the basis of the results of a structural study of the zeolite L–benzene system by powder neutron diffraction.[25] In each segment of the zeolite L channel there are six equivalent sites on the walls of the channel (of type D) for nonframework potassium cations. For the composition of the present zeolite L sample, an average of 4.3 of these sites are occupied by potassium cations. At a loading of approximately 1 benzene molecule per unit cell (or, equivalently, per channel segment) the benzene molecules are observed at 78 K in "capping" positions above these type D potassium cations. The dominant interaction is apparently that between the potassium cation and the π-electron density of the benzene molecule. This interaction is insensitive to rotation of the benzene molecule about the axis connecting its centroid to the potassium cation. Further, the matching between the barrel of the zeolite L channel and the benzene molecular size is such that rotation of the benzene molecule in the molecular plane is not significantly hindered by interaction with the framework oxygen atoms (Figure 2). A simple atom–atom potential modeling of the activation barrier to benzene molecule rotation based on the observed structural data gives a peak to trough energy difference of <1 kcal mol^{-1}.

For 150 K ≤ T ≤ 350 K, although there is no narrow central component that would indicate the presence of an isotropically moving fraction of benzene molecules, the spectra do show significant temperature dependence. First, the magnitude of the effective quadrupolar coupling constant is reduced at higher temperatures (Figure 3), suggesting that the reorientation axis itself is undergoing small precessive motion; that is, the benzene molecules are rocking slightly about the K^+ cation to ring center vector. The rate of reduction in $(e^2qQ/h)_{eff}$ with temperature

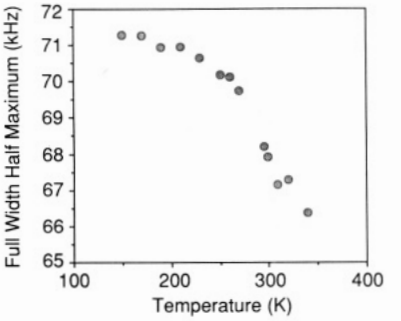

Figure 3. Variation of full width at half-maximum of ^2H NMR signal with temperature for C_6D_6 in zeolite L at a loading level of 1 molecule per unit cell.

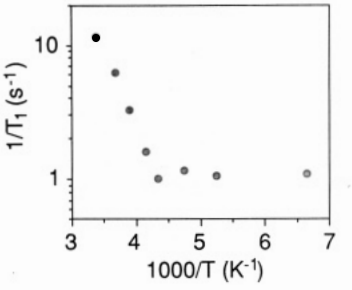

Figure 4. Variation of reciprocal of spin–lattice relaxation time (T_1) with temperature for C_6D_6 in zeolite L at a loading level of 1 molecule per unit cell.

increases markedly at ~250 K (Figure 3). At about this same temperature, a less broad component begins to develop between the pronounced "horns" of the spectrum. This new component does not give sharp spectral features,[28] complicating initial attempts at measurement, but optimization of the solid echo pulse sequence has enabled reasonable definition to be achieved. The general shape of this central component is consistent with an activated site hopping of the benzene molecules, presumably between crystallographically equivalent type D potassium cation sites (Figure 2). A simple treatment of the averaging effects of such motion, combined with the molecular plane spinning, gives a distribution of reduction factors, generally consistent with the form of the observed spectra.[28]

Spin–lattice relaxation measurements proved troublesome in this system because of the large width of the absorption. Signal saturation was, however, accomplished by applying an extended comb pulse sequence, and the saturation recovery signal was then acquired in quadrature. The measured T_1 values vary somewhat from position to position across the full spectrum, being typically smaller close to the central region, particularly at lower tem-

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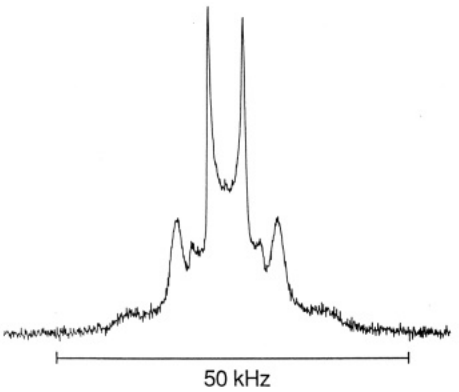

Figure 5. ^2H NMR spectrum for n-C_6D_{14} in zeolite L at 298 K (at a loading level of 1 molecule per unit cell) displaying distinct resonances for the methyl (inner) and methylene deuterons (outer).

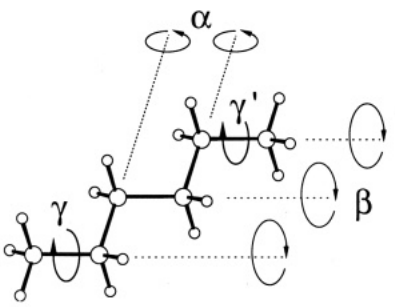

Figure 6. Ball and stick representation of n-hexane illustrating that rotation about two axes (α and β) affects the methylene deuterons, while the methyl deuterons are additionally affected by rotation about a third axis (γ,γ').

peratures. The average of values at the left and right "horns" are plotted in Figure 4. The form of the variation is consistent with the presence of two relaxation mechanisms with differing characteristic activation energies. The crossover point, ~250 K, corresponds to the regime in which the commencement of activated site hopping was, as above, deduced from the shape of the spectra. An activation energy of 4.8 kcal mol^{-1} is inferred from the temperature variation of $1/T_1$ for $T > 250$ K (Figure 4).

Hexane. A typical ^2H NMR spectrum for n-hexane, C_6D_{14}, in potassium zeolite L is shown in Figure 5. There is no narrow central component, indicating that no appreciable fraction of the molecules is free to move isotropically. However, there are two distinct ^2H NMR absorptions with splittings between the principal peaks of 8.26 and 24.79 G. These splittings translate into $(e^2qQ/h)_{eff}$ values of 7.20 and 21.60 kHz, respectively. The ratio between these splittings is precisely 3, although the exact agreement is probably partly fortuitous.

The comparatively small values of $(e^2qQ/h)_{eff}$ imply that a significant degree of motional averaging of the quadrupolar interaction is taking place, most likely in the form of motions involving several degrees of freedom. The previously determined value of $(e^2qQ/h)_0$ for detuerons in an sp^3 bond is 191.5 ± 0.8 kHz,[29] and the ratios of this value to those observed are 26.6 and 8.9, respectively. Such variations involving factors of 3 would be expected if the motion of the hexane molecule were comprised of rotations about the tetrahedral bond angles (Figure 6). For the tetrahedral bond angle, the reduction factor from eq 2 is equal to $-1/3$. For motion of a methylene deuteron, rotation about either of the two adjacent bonds is allowed, and since the reduction factor varies as the product, a ratio of $1/9$ would be expected (Figure 6). For the terminal methyl deuterons, spinning about the 3-fold symmetry axis provides an additional degree of freedom, leading to a total reduction of $1/27$. These numbers are in excellent agreement with the observed ratios. The data indicate that the n-hexane molecules "reptate" within the zeolite and imply a significant interaction between the hydrocarbon and the zeolite cage walls. Similar to the benzene case, the effective quadrupolar splitting for n-hexane is temperature dependent (Figure 7), indicating, largely, additional librational averaging of the spectrum.

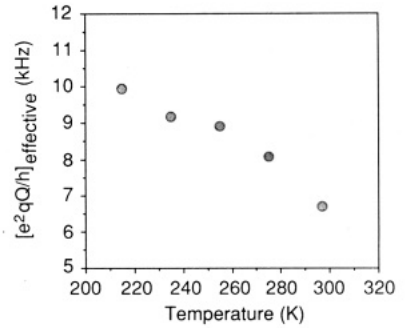

Figure 7. Variation of effective quadrupolar coupling constant (calculated as $^4/_3$ of peak splitting) with temperature for n-C_6D_{14} in zeolite L at a loading level of 1 molecule per unit cell.

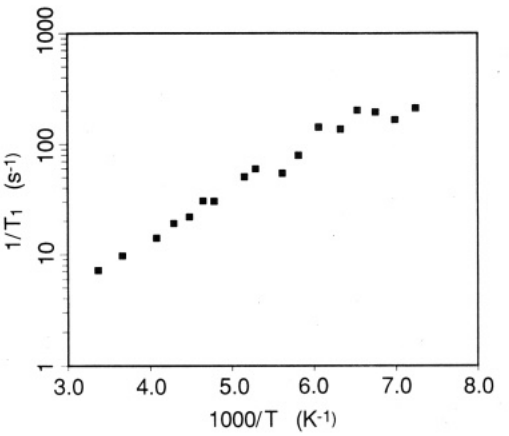

Figure 8. Spin–lattice relaxation data for n-C_6D_{14} in zeolite L (at a loading level of 1 molecule per unit cell) indicating a thermal activation energy of $D \sim 1.95$ kcal mol^{-1} (computed from the linear region $T > 150$ K).

Spin–lattice relaxation times, T_1, were measured as a function of temperature from 293 to 140 K. The variation of the logarithm of $1/T_1$ as a function of $1/T$ (Figure 8) is linear throughout most of the temperature range, with some evidence for leveling out in the vicinity of 150 K. The decline in $1/T_1$ with temperature indicates that we are operating in the regime of eq 3 in which $\omega_0\tau_c \ll 1$, so that $1/T_1 \propto \tau_c$. In this regime a room temperature value of $1/T_1 = 7.2$ s^{-1} corresponds to a short correlation time, $\tau_c = \sim 1.4 \times 10^{-11}$ s (if the motion implied in eq 3 determines T_1). This short value of τ_c strongly suggests that the motion responsible for relaxation is not related to rotation or translation of the molecule as a whole. If the motion responsible for the relaxation is thermally activated, the correlation time will vary as $1/\tau_c = C \exp\{-D/kT\}$, where D is the activation energy for the motion and C is the preexponential factor. An activation energy of $D = 1.95$ kcal mol^{-1} for the molecular motions responsible for the relaxation in n-hexane was determined from the linear regime, $T > 150$ K (Figure 8). This value is comparable to that determined for hindered torsional vibrations in ethane.[30] Both the effective quadrupolar coupling constants and the relaxation properties thus yield a self-consistent picture of the molecular motion.

Cyclohexane. In the two cases discussed thus far, the shape of the ^2H NMR absorption spectrum shows only relatively subtle temperature dependence over the range of observation. This is not the case for cyclohexane (Figure 9). At 296 K the spectrum is relatively broad, with evidence of some unresolved fine structure. In contrast, the 280 K spectrum is narrow and consists of only a central component (expected for isotropic molecular motion).

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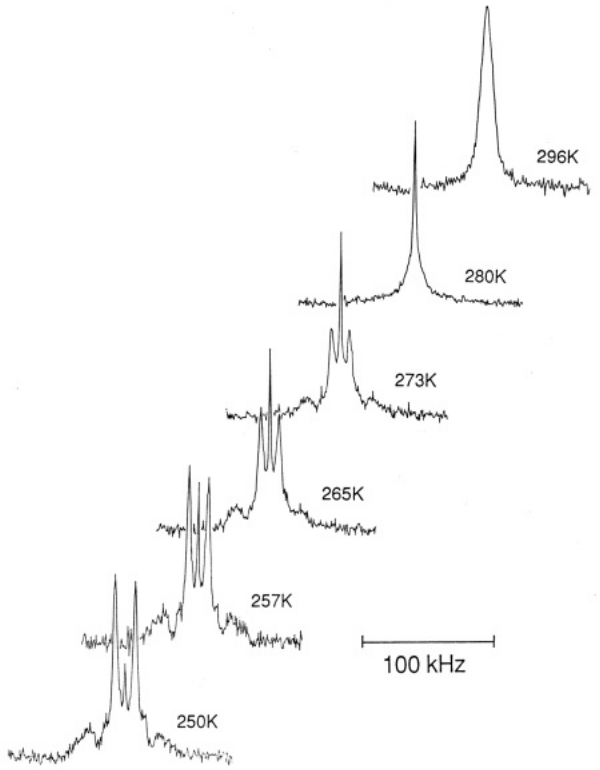

Figure 9. Representative spectra for C_6D_{12} in zeolite L (at a loading level of 1 molecule per unit cell) in the temperature range 296 K ≥ T ≥ 250 K showing narrowing of the line near 280 K and disappearance of the central component below 265 K.

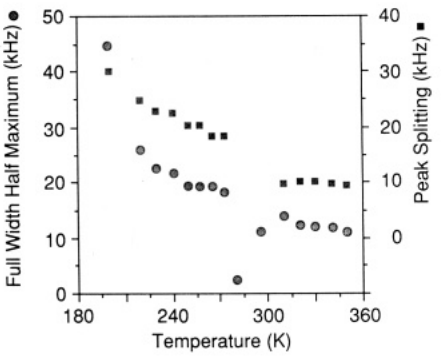

Figure 10. Temperature dependences of full width at half-maximum and of peak splitting for C_6D_{12} in zeolite L (at a loading level of 1 molecule per unit cell).

The intensity of this narrow component diminishes rapidly at lower temperatures, approaching zero around 233 K. "Satellite" lines appear at ~273 K and grow in intensity as the temperature is lowered. The splitting between the "horns" of the spectra increases with decreasing temperature (Figure 10). A plot of T log (I), where I is the integrated NMR signal intensity, against $1/T$ over the full temperature range was flat, demonstrating that the experiment is consistently sampling all of the deuteron spins.

The $(e^2qQ/h)_0$ value for cyclohexane is 173.7 ± 1.7 kHz.[32] The measured values of $(e^2qQ/h)_{eff}$ are plotted as a function of temperature in Figure 10. At 296 K the value of 5.92 kHz is roughly $^1/_{30}$ of the static value. Below the transition region, the value of 11.5 kHz is ~$^1/_{15}$ of the static value. As discussed for the hexane case, free reorientation about two sp^3 C–C bonds would lead to a reduction of the quadrupolar coupling of one-ninth, so additional factors must also be in effect here. Vibrational averaging can also play a role and reorientation of the molecule as a whole will also

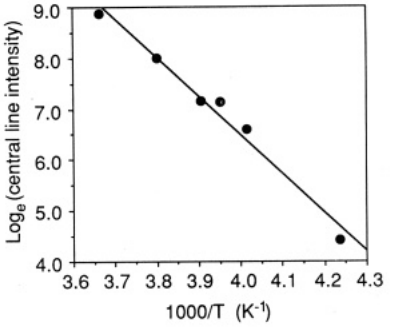

Figure 11. Activation analysis for disappearance of the narrow signal for C_6D_{12} in zeolite L (at a loading level of 1 molecule per unit cell), indicating D = 13.6 kcal mol^{-1}.

contribute to the averaging. In light of the almost complete reduction of the quadrupole interaction in the vicinity of 280 K, such free molecular rotation must be operative in that temperature range. Also important is the steady increase of ΔH_Q with decreasing temperature for T < 260 K (Figure 10). This complicates the process of inferring motions from $(e^2qQ/h)_{eff}$ since there is considerable ambiguity in determining the intrinsic value associated with a particular degree of freedom. However, the approximately linear variation observed here might be expected as a result of torsional or "rocking" motions of the molecule.

A semilogarithmic plot of the ^{2}H NMR signal intensity of the central component as a function of inverse temperature reveals a linear variation, as expected for a thermally activated process (Figure 11). From the slope we infer an activation energy of 13.9 kcal mol^{-1}. This is significantly larger than we would expect on the basis of the energies of motion in liquid C_6D_{12}, for which an activation energy of several kcal mol^{-1} would be expected.[33]

The cyclohexane molecule has two favored conformations, "boat" and "chair". The exchange times between these conformations are on the order of 1 μs at 273 K, exactly the rate at which the ^{2}H NMR line shapes are narrowed by motional processes. The activation energy for the conformation inversion is 11 kcal mol^{-1},[31] close to the value of 13.6 kcal mol^{-1} determined from the temperature dependence shown in Figure 11. The data imply that the strength of the zeolite–sorbate (or, possibly, sorbate–sorbate) interaction is sensitive to the rate at which chair–boat–chair conformation inversions are taking place. The different characteristic energies associated with the conformation inversions and with the zeolite–hydrocarbon interaction will give rise to differing temperature dependences. The data (Figure 10) suggest that these give rise to a temperature window in which the inversion is quenched, but the zeolite–hydrocarbon interaction (which is weaker than in the *n*-hexane case) is insufficient to dampen sufficiently reorientational motion. Although this is a plausible explanation for the ^{2}H NMR properties observed here, further experiments are required in order to quantify the relative strengths of the interactions responsible for this interesting behavior.

Conclusion

The molecular motions of perdeuterated benzene, hexane, and cyclohexane are subject to significant constraints when sorbed at loading levels of 1 molecule per unit cell in potassium zeolite L. For T < ~150 K, benzene gives a well-articulated spectrum with a quadrupolar splitting of half of the static value, interpreted in terms of rapid reorientation within the molecular plane. Combined with low temperature structure results, this mode of reorientation is consistent with a dominating interaction between the ring π-electron density and a type D channel wall potassium cation, with only a limited activation barrier to ring rotation. For temperatures above ~250 K, the development of a less broad component indicates an activated hopping of benzene molecules between different sites. The two distinct spectral components observed for *n*-hexane are attributed respectively to the methyl and methylene

(31) See, e.g.: Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; W. A. Benjamin: New York, 1965; pp 103–109.

(32) Barnes, R. B. In *Advances in Nuclear Quadrupole Resonance*; Smith, J. A. S., Ed.; Heydon: London, 1974; p 335.

(33) See, e.g.: Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; p 138.

deuterons; the quadrupolar splittings can be interpreted in terms of molecular reptation involving torsional rotations about the carbon–carbon bonds. Cyclohexane unexpectedly shows a transition in the dynamical behavior (on the time scale of the ^2H NMR experiment) in the vicinity of 280 K. The narrow signal observed at 280 K is consistent with effectively isotropic reorientations, but the considerably broader spectra observed at both higher and lower temperatures indicate significant residual quadrupole interactions and, hence, more constrained motion. The motions observed for perdeuterated benzene, hexane, and cyclohexane in zeolite L at the present loading level of 1 molecule per unit cell illustrate differing degrees of competition between interaction with the zeolite and internal vibrational modes. It will be interesting to explore the effects on these motional properties of sorbate–sorbate interactions (at higher loading levels), of changes in the zeolite composition, and of altered zeolite pore geometry.

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Influence of Pressure and Electrolyte on the Phase Behavior of Water + Oil + Nonionic Surfactant Systems

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The influence of pressure and the lyotropic electrolyte sodium chloride on the phase behavior of water + oil + nonionic surfactant systems was studied. Various phase transitions were observed visually in mixtures of water + phenylalkanes + *n*-alkyl polyglycol ethers over a temperature range of 280–365 K and a pressure range of 0.1–100 MPa (incidentally, pressures up to 300 MPa were used). Results show that the three-phase region in which three liquid phases are in equilibrium widens with increasing pressure and temperature. At constant temperature phase behavior of the type $\bar{2}$–3–$\underline{2}$ was found with increasing pressure. Furthermore, it is shown in systems which *do not* have a three-phase region at atmospheric conditions that such a region can be induced by increasing the pressure or by adding sodium chloride.

I. Introduction

Mixtures of the type H_2O + oil + surfactant are applied in several industrial processes, e.g., the production of drugs, herbicides, and insecticides and in the food industry.[1] They are also important in the oil industry when surfactants are used to recover residual oil, a process which is often referred to as surfactant, micellar, or microemulsion flooding.[2,3] Several research groups have studied the phase behavior of H_2O + oil + surfactant systems; we refer, e.g., to the work of Shinoda and Kunieda,[4-7] Kunieda and Friberg,[8] Kahlweit and Strey,[9] and Bellocq et al.[10] It was shown by the Japanese group[11] and by the group of Kahlweit[12] that the possible appearance of a three-phase region in which three liquid phases are in equilibrium can be looked upon as a near-tricritical phenomenon. Actually Kunieda and Shinoda[13] found tricritical phenomena in the system sodium taurocholate + water + sodium chloride + glycerol mono(2-ethylhexyl) ether + glycerol tris(2-ethylhexanoic) ester and Kahlweit et al.[14] reported a tricritical point in the system H_2O + phenylhexane + phenylheptane + 2-(2-butoxyethoxy)ethanol.

In particular the group of Kahlweit[12] performed a systematic investigation on the phase behavior of H_2O + oil + nonionic surfactant systems. They also studied the influence of electrolytes and ionic surfactants (surface-active electrolytes) on the phase behavior of these systems.[15]

However, all these measurements were performed at atmospheric conditions and until now little is known about the influence of pressure on the phase behavior of H_2O + oil + surfactant systems except for the work of Fotland,[16] Kim et al.,[17] and Kim and O'Connell.[18] They studied the influence of pressure on quinary surfactant systems consisting of H_2O + oil + nonionic surfactant + ionic surfactant + electrolyte. Systems of this type, which appear to have a three-phase region where the interfacial tension between the different phases can reach extremely low values (<0.001 mN m^{-1}),[18] are often used as a model system for surfactant flooding. The outcome of a systematic investigation on the influence of pressure on the phase behavior of this type of systems can be important, particularly in the process of surfactant flooding where the pressure is a function of the reservoir depth and can easily extend to 40 MPa or even more. Very recently Kahlweit et al.[14] published in a review article some high-pressure data for H_2O + oil + nonionic surfactant systems.

In this paper the results of a study on the influence of pressure on a subsystem of the quinary system namely the system H_2O + oil + nonionic surfactant are presented. Phenylalkanes were

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