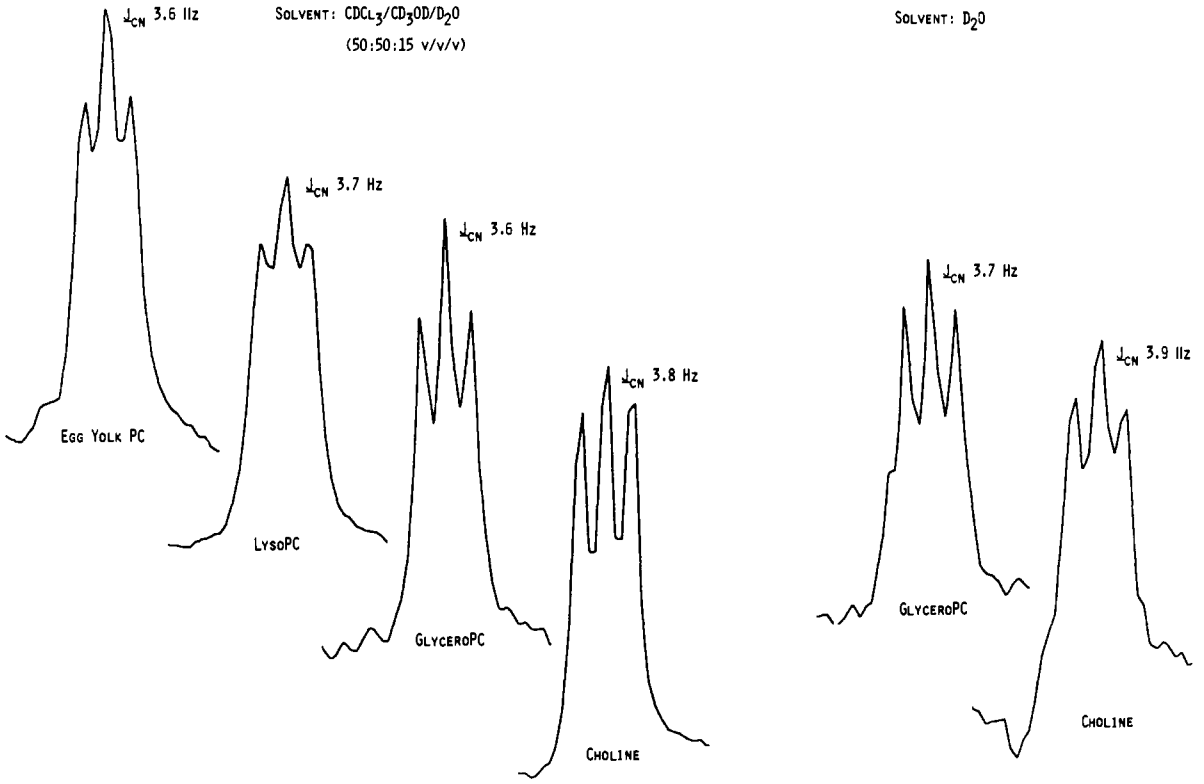

Figure 2. Line shape of $N(CH_3)_3$ signals ($J_{CN} \pm 0.1$ Hz) of choline derivatives in proton-decoupled 20-MHz ^{13}C NMR spectra[7] of egg yolk PC (**1**), LysoPC (**2**),[10] GlyceroPC (**3**),[11] and choline chloride in $CDCl_3/CD_3OD/D_2O$ (50:50:15, v/v/v)[8] and in D_2O.

dipolar broadening or a decrease in ^{14}N relaxation times.

In order to differentiate between the two effects, we measured ^{14}N T_1 and T_2* values of several choline derivatives in various solvents (Table I).[13] As one would expect, T_1 values of compounds in solution decreased with increasing molecular size in a given solvent, for example, in the series choline, GlyceroPC, LysoPC, PC in CMW-*d*[8] or similarly in CD_3OD. Further reduction in relaxation time, for example, for PC in D_2O (0.06 s) vs. CMW-*d* (0.136 s), can be attributed to liposome formation; reverse-micellar aggregation causes a similar reduction in relaxation times as is shown for PC in $CDCl_3$ (T_2* = 0.041 s)[13] vs. CMW-*d* (T_1 = 0.136 s) or CD_3OD (T_1 = 0.150 s) (Table I).

From the observed $^{13}C-^{14}N$ couplings of $N(CH_3)_3$ in solution, which average 3.7 Hz (Figure 2 and ref 15), and the limiting conditions $\eta^2 = 10^2$ at which broadening of the triplet begins,[4] T_1 of ^{14}N can be calculated according to eq 1. The calculations predict that triplet broadening would occur for T_1 values shorter than 0.086 s which would lead to the eventual collapse of the splittings. The ^{14}N relaxations for various choline derivatives (Table I) and the line shapes of the respective $N(CH_3)_3$ signals (Figures 1 and 2) are consistent with these calculations. This also demonstrates that nonobservation of C-N splittings can well be rationalized on the basis of a reduction in ^{14}N T_1 alone rather than by dipolar broadening.[16]

From our data we conclude that restrictions in mobility of the CH_2-CH_2 bond, that affect the CH_2-N vector, can be attributed to polar headgroup interactions. ^{14}N T_1 values and J_{CN} couplings are diagnostic of headgroup association and should prove useful in monitoring changes in the state of aggregation of choline phospholipids.

Acknowledgment. This study was supported in part by U.S. Public Health Service Research Grant HL 08214 from the Program Projects Branch, Extramural Programs, National Heart, Lung and Blood Institute, USPHS Research Grant NS 14304 from the National Institute of Neurological and Communicative Disorders and Stroke, and The Hormel Foundation. We are particularly grateful to Dr. S. Parthasarathy for preparing the choline derivatives used in this study.

(13) It has previously been noted that for reverse micelles of PC, T_2* is only slightly shorter than T_1, and hence either value can be used for approximating ^{14}N correlation times.[14]

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(15) $J_{^{13}C-^{14}N}$ values (±0.1 Hz) were for egg yolk PC (**1**), CD_3OD, 3.4 Hz, CMW-*d*,[8] 3.6 Hz; LysoPC (**2**), CMW-*d*, 3.7 Hz; choline chloride, CD_3OD, 3.9 Hz, CMW-*d*, 3.8 Hz, D_2O, 3.9 Hz.

(16) Observation of $N(CH_3)_3$ triplets in ^{13}C spectra of PC vesicles at elevated temperature[6] could be related to the increase in surface area per molecule with temperature[17] which would result in faster CH_2-CH_2 rotation and longer ^{14}N T_1 values due to decreased headgroup interactions. Koga and Kanazawa[14] also found that above 60 °C the T_1 values of PC vesicles were greater than the 0.086 s which we have calculated.

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NMR Investigation of a Surface Compound on Colloidal Silica

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Received July 9, 1980

Adsorption of inorganic and organometallic compounds on the surfaces of oxides is a process of fundamental importance in the preparation and operation of heterogeneous catalysts. Investigation of such systems by nuclear magnetic resonance is nontrivial, because restricted molecular motion in the solid state frequently leads to nonaveraged static interaction[1] although workers using Magic-angle spinning and multiple pulse techniques have made significant contributions to this area.[2-4] We wish to report a novel approach which uses NMR as a surface-sensitive technique in fluid

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0002-7863/81/1503-1240$01.25/0

media and the observation of high-resolution ^{19}F NMR spectra of a chemisorbed compound.

We reasoned that if the oxide surface could be subdivided sufficiently, the resulting particles, when dispersed in a suitable fluid, would exhibit correlation times short enough to allow observation of NMR spectra of surface phase(s). This describes, in a limiting case, a colloid, and we have used as the oxide adsorbent colloidal 350 Å mean diameter silica particles in 2-ethoxyethanol (EEO).[5] The silica has a surface area of 150 M^2 gm^{-1} and is amorphous to electrons. The iron content, determined by emission spectrography, is 3 ppm. The adsorbate studied is palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$. This fluorinated organometallic compound is a strong Lewis acid and readily forms complexes with a wide variety of molecular and condensed phase donors.[6,7] For the purpose of preparation and study of surface compounds, it offers several advantages: (1) there is high Lewis acidity; (2) the molecule contains 12 fluorines per acidic metal site; (3) the ^{19}F chemical shifts are sensitive to chemical environment; (4) spin rotation and dipole–dipole relaxation in the CF_3 groups are expected to be efficient even when the molecule is bound to the surface of a particle.

The 94.1-MHz Fourier transform ^{19}F spectrum of a 1.3×10^{-2} M solution of $Pd(F_6acac)_2$ in the silica colloid exhibits a sharp peak at 73.32 ppm (w/2 1.8 Hz, relative area 1) whose position and width are the same as that of $Pd(F_6acac)_2$ in EEO. In addition, a broad peak at 75.4 ppm (w/2 21 ± 2 Hz, relative area 0.6) is observed in the colloid–EEO but not in pure solvent. Such an upfield shift is typical of Lewis base adducts of $Pd(F_6acac)_2$,[6] and we attribute this new resonance to a complex between $Pd(F_6acac)_2$ and basic site(s) on the surface of the colloidal particles. The observation of separate peaks for free and bound $Pd(F_6acac)_2$ indicates that the exchange between these two forms is not rapid on the NMR time scale. In this system, which has a kinematic viscosity of 5.50 cSt,[8] the ^{19}F spin–lattice relaxation time, T_1, of the fluorines in free $Pd(F_6acac)_2$ is 1.01 s and that of the surface-phase fluorine is 0.26 s. When the viscosity is reduced to 3.55 cSt by dilution with pure EEO, T_1 for the free and bound forms are 0.87 and 0.24 s, respectively.

If the T_1/T_2 ratio as described by Navon and Lanie[9] is used and it is assumed that an intramolecular dipole–dipole relaxation mechanism is dominant, τ_C for the fluorines in the $Pd(F_6acac)_2$ surface compound was calculated to be 4×10^{-9} s. This is much shorter than the 3×10^{-5} s overall correlation time for tumbling of a particle of 175-Å radius[11] and is indicative of fast reorientation of the axially symmetrical CF_3 groups. This provides a relaxation mechanism which is not dependent on motion of the small particles bearing the surface compound. The observed magnitude of T_1 is reasonable for a trifluoromethyl group in a surface phase bound for times longer than $(2\pi\Delta\nu)^{-1}$ but in which internal rotation is almost free, and so we defer consideration of more complex models of anisotropic rotation. Minimal importance of particle motion as a determinant of T_1 is also indicated by the absence of a dependence of T_1 on the viscosity of the medium.

T_2 and intrinsic line width are related by $T_2 = \pi\nu_{1/2}$ where $\nu_{1/2}$ is the full width (in Hz) at half-height of a peak.[10] The line width of the bound $Pd(F_6acac)_2$ peak in the spectra obtained at 188.2 MHz is 58 Hz. Direct measurement of T_2 (Carr–Purcell Meiboom–Gill pulse sequence) gave T_2 for this peak as 0.026 ms; so the intrinsic line width is 12 Hz. Therefore, the linewideth of the bound $Pd(F_6acac)_2$ may reflect chemical heterogeneity of the silica surface and residual intramolecular broadening. Adsorption of $Pd(F_6acac)_2$ to a colloidal particle is analogous to the absorption of a fluorine-labeled amino acid on a protein. Thus, T_1 and T_2 of the surface phase are comparable to T_1 and T_2 of the CF_3 group in *N*-trifluoroacetyltryptophan-*d* bound to α-chymotrypsin.[11a-c]

It seemed plausible that if NMR spectra can easily be obtained from a surface compound on a colloidal support, it ought to be possible to obtain the spectrum of the colloid itself. The ^{29}Si NMR spectrum (39.7 MHz, 10K transients) of the silica colloid consists of a broad (w/2 650 Hz) resonance 105 ppm upfield of external $(CH_3)_4Si$. In this experiment, we are observing silicon at or near the surface because T_1 for ^{29}Si buried in the colloidal particles should be very long. For example, T_1 is at least 12 h for dipole–dipole relaxation in a 175-Å particle, assuming only rotational motion.[12] The only ^{29}Si nuclei observable in the NMR are probably those on the outside of the sphere which can be relaxed by protons from the solvent, or which participate in chemical reactions, such as exchange of silanol protons or equilibrium solvolysis of siloxane linkages.

We believe that, in suitable cases, colloids will constitute useful models for bulk oxides and that nuclear magnetic resonance will be a useful tool for the study of surfaces of colloidal materials and chemical compounds formed on them.

Acknowledgment. We are grateful to S. Shiffman and P. F. Cullen for the electron miscroscopy and viscosity measurements, A. Cirillo for helpful discussion, and W. C. Jankowski of Varian Associates for the 188-MHz spin–spin relaxation time measurements.

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Structures of BBM-928 A, B, and C. Novel Antitumor Antibiotics from *Actinomadura luzonensis*

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Received October 10, 1980

In the course of our antibiotic screening program, a complex of potent antitumor agents designated BBM-928 was isolated from the culture broth of *Actinomadura luzonensis* nov. sp.[1,2] BBM-928 resembles the quinoxaline group of antibiotics, which include actinoleukin,[3] echinomycin,[4] and quinomycins,[5] in that they are all cyclic depsipeptides having two chromophoric units in the structure. However, BBM-928 differs from the latter group in the chromophore structure and by virtue of the lack of a sulfur-containing cross-linkage. In the present communication we report the structures of BBM-928 A (**1a**), B (**1b**), and C (**1c**) (Figure 1).

BBM-928 A (**1a**) ($C_{64}H_{78}N_{14}O_{24}$, mp 246–248 °C, $[\alpha]^{25}_D$ −27°)[6] and BBM-928 C (**1c**) ($C_{60}H_{74}N_{14}O_{22}$, mp 244–248 °C, $[\alpha]^{25}_D$ −91°) were isolated as major components, while BBM-928

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0002-7863/81/1503-1241$01.25/0