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Group Contribution Analysis of Xenon NMR Solvent Shifts

Michel Luhmer* and Kristin Bartik

Chimie Organique, CP 165, Université Libre de Bruxelles, Av. F.D. Roosevelt, 50, 1050 Brussels, Belgium

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^{129}Xe gas-to-solution NMR chemical shifts for xenon dissolved in pure *n*-alkanes, *n*-alkyl alcohols, *n*-alkyl carboxylic acids, di-*n*-alkyl ketones, and cycloalkanes and in solutions of lauric acid in *n*-heptane are reported. The medium effect corrected for solvent density is found to be linearly dependent on the number of carbon atoms except for the shortest members of the series of linear solvents. The same slope is observed for all the linear solvents; the slope for the cycloalkanes is significantly different. These results are interpreted on the basis of a group contribution analysis. The relative contribution of methyl and methylene groups in linear solvents is found to be in very good agreement with the relative Xe−CH$_3$ and Xe−CH$_2$ dispersive interaction energies. The ^{129}Xe chemical shifts for solutions of lauric acid in *n*-heptane calculated from the group contributions are in excellent agreement with the experimental values. The deshielding effect of the methylene group in cycloalkanes and the ^{129}Xe chemical shift measured in the shortest members of the linear series of solvent are discussed in terms of intermolecular shielding functions and distributions of groups in the solvation shell of the Xe atom.

Introduction

Two xenon isotopes are easily accessible to nuclear magnetic resonance (NMR) spectroscopy: ^{129}Xe ($I = {}^1/_2$, natural abundance of 26.4%) and ^{131}Xe (${}^3/_2$, 21.2%).[1] The NMR parameters of these isotopes are very sensitive to the environment of the xenon atom, and analysis of the literature indicates that monatomic xenon has attracted much attention as a sensitive indirect probe of structural and dynamical properties of molecules in gas mixtures, simple liquids, isotropic and anisotropic solutions, biological systems, and various solid materials.[2−5] The emergence of highly polarized ^{129}Xe obtained by optical pumping techniques has increased the importance of Xe NMR spectroscopy,[5,6] and new applications, such as ^{129}Xe NMR imagery, are being developed.[7−10]

The observed range of chemical shifts for monatomic xenon dissolved in simple liquids is 250 ppm;[4] this clearly illustrates the high sensitivity of the xenon screening constant to the environment. Since the pioneering work of Buckingham and co-workers,[11] it is known that the screening constant of a nucleus, σ, is the sum of the screening constant in the isolated molecule, σ°, and a term due to the presence of the solvent. It is important to distinguish in the solvent term the contribution due to the bulk magnetic susceptibility of the sample, σ_b, from the *true* medium effect, σ_m, which arises from solute−solvent interactions (eq 1a). In the absence of strong specific solute−solvent interactions leading to supramolecular assemblies, the medium effect can be described as a sum of four terms (eq 1b): (i) σ_a, the contribution arising from anisotropy in the molecular magnetic susceptibility of the solvent molecules, (ii) σ_w, the shielding due to the van der Waals solute−solvent interactions, (iii) σ_e, the contribution arising from electrostatic interactions between solvent and solute permanent electric moments, and (iv) σ_{e2}, the contribution due to the interactions between the solvent permanent dipoles or higher multipoles and the solute induced dipole.

$$\sigma = \sigma^\circ + \sigma_b + \sigma_m \qquad (1a)$$

$$\sigma_m = \sigma_a + \sigma_w + \sigma_e + \sigma_{e2} \qquad (1b)$$

The gas-to-solution chemical shift of xenon is dominated by the dependence of σ_w on the environment of the xenon atom. Indeed σ_b and σ_a lie in the ppm range and σ_e is zero for neutral monatomic species. The σ_{e2} contribution could play a role in the case of xenon, a highly polarizable solute, dissolved in solvents made of small polar molecules but is not expected to be dominant since Debye energies are always smaller than London interaction energies.[12] Furthermore, in the case of neon it has been shown that this contribution is indeed negligible in front of the van der Waals term.[13]

Attempts to interpret ^{129}Xe NMR solvent shifts have frequently been based on the reaction field theory of Onsager[14] which describes the solvent as a continuum. The model developed by Rummens[15,16] leads to a search for correlations between σ_w and the square of the function $g(n) = (n^2 - 1)/(2n^2 + 1)$, where n is the refractive index of the pure solvent. This approach, and more sophisticated reaction field models, can in part account for ^{129}Xe NMR solvent shifts[17−21] but offer little insight into the intermolecular interactions that give rise to these solvent shifts. To overcome these limitations, it is necessary to adopt a microscopic description of liquids and solutions in order to account for their discrete nature. This requires information on the local arrangement of solvent molecules around the solute. In a previous work on ^{129}Xe NMR solvent shifts,[22] we proposed to use a simplified analytical form for the solute−solvent molecular pair distribution function (the PISA model) and to take Xe−solvent pair interactions explicitly into account using atom−atom (atom−site) pair potentials. This led us to conclude that the ^{129}Xe NMR solvent shift is directly proportional to the Xe−solvent London energy, which is better estimated via the PISA model than via the reaction field theory. The use of molecular dynamics (MD) simulations and Monte Carlo (MC) techniques for investigating properties of condensed phases is now well-established. In the context of Xe NMR, computer simulations have led to a better understanding of the relaxation of ^{131}Xe dissolved in various solvents[23−26] and have confirmed the significance of the intermolecular dipole−dipole

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* Corresponding author. E-mail: mluhmer@ulb.ac.be; kbartik@ulb.ac.be. Fax: +32 2 650 36 06.

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spin-relaxation mechanism for ^{129}Xe in benzene.[27] Jameson et al.[28] carried out grand canonical ensemble MC simulations of Xe atoms trapped in the α cages of zeolite NaA, and it is very interesting to note that the experimental ^{129}Xe chemical shifts of Xe clusters and their temperature dependence are reproduced quantitatively by the simulations. These chemical shift calculations were made using pairwise additive ab initio intermolecular shielding functions calculated for argon model systems and scaled to Xe−Xe and Xe−zeolite atom pairs.[29] They calculated a distance dependence of the atom−atom shielding functions which is close to r^{-6} for the distances most frequently sampled in the liquid phase, i.e., the distances near or beyond the sum of the van der Waals radii. In previous work we found a correlation between the gas-to-solution xenon NMR shifts and the xenon−solvent-dispersive interaction energy estimated using the PISA model[22] or MC simulations.[30] Lau and Gerig[13] used MD simulations to calculate the ensemble average of Ne-atom shielding functions that exhibit a r^{-6} or $r^{-6.5}$ distance dependence and found a very good correlation between calculated and experimental medium effects on the ^{21}Ne gas-to-solution NMR shifts. Recently, Lim et al.[31,32] interpreted the NMR solvent shift for ^{129}Xe dissolved in *n*-alkanes, in long-chain alcohols, and in primary *n*-alkylamines in terms of pairwise interactions between Xe atoms and the solvent constituent groups (CH_3-, $-CH_2-$, $-NH_2$, and $-OH$). They found the deshielding produced by methyl groups to be much smaller than the effects produced by methylene, amino, or hydroxyl groups. They emphasized that they results suggest that the dispersion force interactions between Xe atoms and CH_3- groups are weaker than those involving Xe and $-CH_2-$ and pointed out that this differs from conclusions drawn elsewhere.

In our ongoing effort to interpret ^{129}Xe NMR solvent shifts, we have measured ^{129}Xe chemical shifts for xenon dissolved in various solvents and in binary solutions, and interpreted the data on the basis of a group contribution analysis. This work has been performed with the aim of proposing a set of functional group contributions to the ^{129}Xe gas-to-solution NMR shifts that are consistent with dispersive interaction energies and that can be used to build a library of transferable intermolecular shielding functions.

Materials and Methods

Xenon gas at natural abundance was purchased from Air Liquide. The liquid solvents were purchased from various suppliers and used without further purification (quoted purity greater than 98%); hygroscopic liquids were however dried on molecular sieves. Solutions were prepared by weighing in 5 mL volumetric flasks.

For the measurement of ^{129}Xe NMR chemical shifts, samples of approximately 2 mL were placed in a 10 mm NMR tube, and xenon was bubbled through the samples with a capillary for 5−10 min at room temperature. For lock and external referencing purposes, a sealed 5 mm NMR tube containing xenon dissolved in acetone-d_6 was inserted coaxially into the 10 mm NMR tube. The 10 mm tube was then capped and sealed with Teflon tape. NMR spectra were recorded at 293 K on a Bruker AMX360 spectrometer (nominal frequency for ^{129}Xe = 99.615 MHz) equipped with a standard 10 mm broadband probe. For the chemical shift measurements, eight scans were recorded for each spectrum using a 5 μs (30°) pulse, a 4 s repetition time, a center-band frequency of 99.632 MHz, and a spectral width of 5000 Hz. Digital resolution was 0.125 Hz/point after two levels of zero filling. Spectra were weighted with an exponential line-broadening of 1 Hz; the resulting line widths never exceeded 2 Hz for the reference signal and 3.5 Hz for xenon in the various solvents.

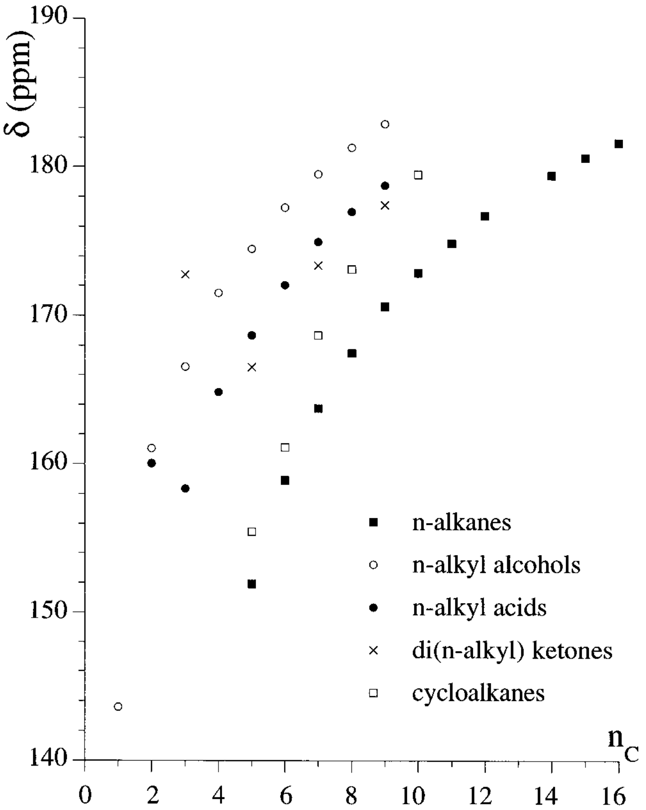

Figure 1. ^{129}Xe gas-to-solution NMR chemical shifts at 293 K displayed as a function of the number of carbon atoms (n_C) in the solvent molecules. δ values are referenced to the resonance frequency of xenon gas extrapolated to zero pressure.

The resonance frequency of xenon in the 5 mm reference tube was calibrated with respect to the resonance frequency of xenon gas extrapolated at zero pressure. The latter was obtained from a series of nine NMR frequency measurements for xenon gas at pressures ranging between ca. 2 and ca. 10 atm. Xenon was condensed in an evacuated 10 mm heavy-walled NMR tube (ca. 7 mL capacity) equipped with a pressure valve. The quantity of xenon was known precisely from weighing. These NMR measurements were performed without lock. The shim were set up by optimizing the ^{1}H FID signal for acetone vapors and were not changed during the whole series of xenon gas NMR measurements (eight scans, 30° pulses, repetition delay of 10 s). The line width of the ^{129}Xe signal never exceeded 2 Hz.

Results

The chemical shift of xenon dissolved in the various solvents were measured at 293 K and were referenced to the resonance frequency of xenon gas extrapolated to zero pressure; thus $\delta = -(\sigma_b + \sigma_m)$. They are displayed in Figure 1 as a function of the number of carbon atoms (n_C) in the solvent molecules. As observed elsewhere,[31] δ increases with carbon number in a nonlinear manner. The shortest member of the acid and ketone series deviate from the general trend, however. Values for σ_b were calculated according to eq 2 using data found in the

$$\sigma_b = -\frac{4\pi}{3}\chi_v = -\frac{4\pi}{3}\rho\chi_M \qquad (2)$$

literature: molar magnetic susceptibility (χ_M)[33] and pure solvent density (ρ in mol L^{-1}, derived from d^{20} values).[34] The *true* medium effects on the ^{129}Xe chemical shift, $-\sigma_m = \delta + \sigma_b$ (σ_m is negative) display a similar trend as the data in Figure 1,

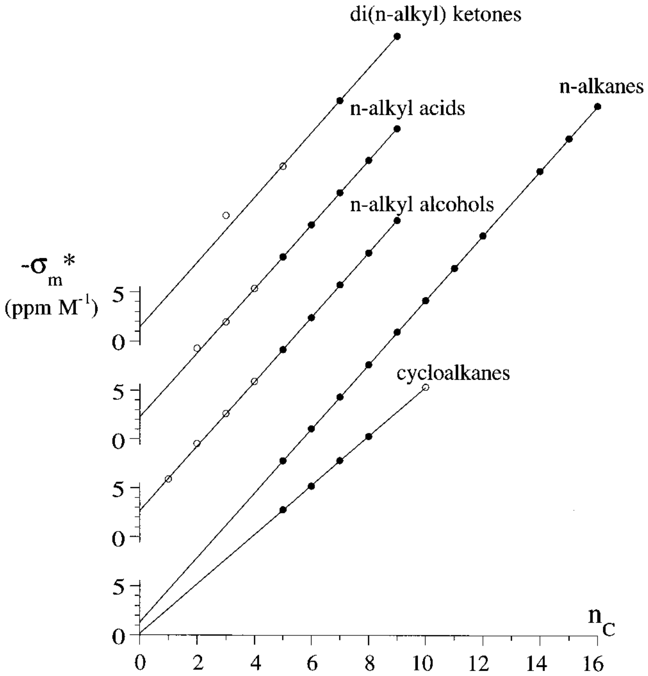

Figure 2. Molar medium effect on the ^{129}Xe gas-to-solution NMR chemical shifts at 293 K displayed as a function of the number of carbon atoms (n_C) in the solvent molecules. Open points correspond to solvents not included in the linear fitting procedure of $-\sigma^*_m$.

with the same deviations for the shortest member of the acid and ketone series.

In the pairwise additivity theory of isotropic homogeneous fluids,[35] an observable solute−solvent property of a dilute binary system, $\langle B\rangle$, which is *experimentally* the time average of a function of the phase variables (the function is also assumed to be pairwise additive), can be written as

$$\langle B\rangle = 4\pi\rho \int_0^\infty \mathrm{d}r\, r^2 \int \mathrm{d}\Omega\, B(r,\Omega)\, g(r,\Omega) / \int \mathrm{d}\Omega \qquad (3)$$

where r is the solute−solvent intermolecular distance, Ω are the angular variables describing the relative orientation of the solute−solvent pair of molecules, and $g(r,\Omega)$ is the solute−solvent pair distribution function which describes the local arrangement of solvent molecules around the solute. From eq 3, it can be seen that $\langle B\rangle$ is explicitly dependent on the density of the solvent in addition to an implicit dependence of $g(r,\Omega)$ on ρ. The explicit dependence on the density can easily be taken into account and we define the molar medium effect for the ^{129}Xe chemical shift as $-\sigma^*_m = -\sigma_m/\rho$. Values of $-\sigma^*_m$ are displayed in Figure 2 as a function of n_C. In a series of homologous solvents, $-\sigma^*_m$) is found to be essentially linearly dependent on n_C, and, very interestingly, the data for the different series of linear solvents lie on parallel lines. The first observation indicates that the nonlinear dependence of δ on the carbon number of the solvent molecules (Figure 1) is mainly due to the dependence of ρ on n_C. The shortest member of the acid and ketone series still deviate but to a lesser extent than what is observed in Figure 1; comments on the possible origins of these deviations are given in the next section. The linear dependence of $-\sigma^*_m$ on n_C within a series of solvents suggests that it should be possible to analyze the ^{129}Xe chemical shift in terms of group contributions. Assuming pairwise additive Xe−site intermolecular shielding functions (a site can be an atom or a group of atoms), eq 3 can be rewritten for σ^*_m as

$$\sigma^*_m = \sum_s n_s 4\pi \int_0^\infty \mathrm{d}r\, r^2 \int \mathrm{d}\Omega\, \sigma_s(r,\Omega)\, g(r,\Omega) / \int \mathrm{d}\Omega = \sum_s n_s \sigma^*_s \qquad (4)$$

where the summation runs over the nonequivalent sites of the solvent molecule, n_s is the number of sites of type “s”, and $\sigma_s(r,\Omega)$ is the Xe-s intermolecular shielding function (σ^*_m, σ^*_s, and $\sigma_s(r,\Omega)$ are negative). The definition of nonequivalent groups is somewhat subjective. Intuitively, it can be based on the chemical nature of the site. Methylene groups ($-CH_2-$) have then to be distinguished from methyl (CH_3-) or hydroxyl ($-OH$) groups. Whether a $-CH_2-$ group in alkanes is equivalent to a $-CH_2-$ adjacent to a $-OH$ group and how far the neighboring groups have to be taken into account is not clear, however. Sandler and co-workers[36] developed, on the basis of ab initio calculations of electronic charge distributions for various isolated organic molecules, a theoretical basis for defining functional groups that led them to identify, for instance, $-CH_2OH$, $-CH_2COCH_2-$, or $-CH_2COOH$ as basic groups. The number of nonequivalent groups that can be defined in the present study is limited however by the number of parameters characterizing the dependence of $-\sigma^*_m$ on n_C: the slope and the intercept of the straight lines. In the following analysis, methylenes bound to carbon atoms ($-CH_2-$ in $C-CH_2-C$), independently of the nature of the neighboring carbon atoms, are identified as a single group. The remaining functional groups each contain one carbon atom (CH_3-, $-CH_2OH$, $-COOH$, $-CO-$). Taking the total number of carbon atoms in the solvent molecules (n_C) explicitly into account, eq 4 can be rewritten as

$$\sigma^*_m = \sum_{s\neq CH_2} n_s(\sigma^*_s - \sigma^*_{CH_2}) + \sigma^*_{CH_2} n_C \qquad (5)$$

$-\sigma^*_{CH_2}$ is then the slope characterizing the linear dependence of $-\sigma^*_m$ on n_C. Since deviations from linearity are observed for the shortest members of the series, only data corresponding to solvents with at least three $-CH_2-$ groups are included in the linear adjustment procedure. In the case of the di-*n*-alkyl ketone series of solvents, data corresponding to the di-*n*-propyl was however considered. Table 1 gives the results of the fitting procedure. The values for the slope of the lines ($-\sigma^*_{CH_2}$) corresponding to the series of linear solvents range between 3.28 and 3.30 ppm M^{-1} and are considered to be not significantly different from the value estimated for *n*-alkanes: $-\sigma^*_{CH_2} = 3.29$ ppm M^{-1}. The molar contribution of the methyl group, determined from the intercept of the line corresponding to the *n*-alkanes, is found to be $-\sigma^*_{CH_3} = 3.95$ ppm M^{-1}. Since the methylene contribution to the ^{129}Xe chemical shift is found to be identical in the whole set of linear solvents, it is reasonable to make the assumption that the methyl contribution is also identical. The deshielding effect due to the oxygen containing functional groups encountered in alcohols, acids, and ketones ($-\sigma^*_{CH_2OH}$, $-\sigma^*_{COOH}$, and $-\sigma^*_{CO}$), were then obtained from the intercepts using $-\sigma^*_{CH_3} = 3.95$ ppm M^{-1} and $-\sigma^*_{CH_2} = 3.29$ ppm M^{-1} and are listed in Table 1. For the cycloalkane series of solvents, the intercept is not significantly different from zero, as it should be, but the deshielding effect due to the methylene group ($-\sigma^*_{CH_2} = 2.52$ ppm M^{-1}) is much smaller than the value obtained for the set of linear solvents; this observation is discussed in the next section. At this stage, it is worth noting that (i) while the ^{129}Xe chemical shift is larger in cycloalkanes than in the corresponding *n*-alkanes (Figure 1), the molar deshielding medium effect ($-\sigma^*_m$) is smaller in the cyclic solvents (Figure 2); this emphasizes the importance of

TABLE 1: Group Contributions to the Molar Medium Effect on the ^{129}Xe Chemical Shift at 293 K

solvent series	$-\sigma^*_{CH_2}$ (ppm M^{-1})	intercept (ppm M^{-1})	group contributions to the intercept	$-\sigma^*_s$ (ppm M^{-1})
n-alkanes	3.289 ± 0.002	1.33 ± 0.01	$2(S-CH_2)$; $S = CH_3$	3.95 ± 0.01
n-alkyl alcohols	3.299 ± 0.005	2.66 ± 0.04	$CH_3 + S-2CH_2$; $S = CH_2OH$	5.29 ± 0.05
n-alkyl acids	3.277 ± 0.004	2.26 ± 0.03	$CH_3 + S-2CH_2$; $S = COOH$	4.89 ± 0.04
di-*n*-alkyl ketones	3.298	1.47	$2CH_3 + S-3CH_2$; $S = CO$	3.44
cycloalkanes	2.52 ± 0.03	0.17 ± 0.17		

the density effects and (ii) the quality of the linear adjustment of $-\sigma^*_m$ versus n_C is not as good for cycloalkanes as for the set of linear solvents (see Supporting Information).

For xenon dissolved in binary solutions, the ^{129}Xe chemical shift with respect to the resonance frequency of xenon gas extrapolated to zero pressure, $\delta = -(\sigma_b + \sigma_m)$, can be written as eqs 6a and 6b, where [A] and [B] are the molar concentrations

$$\sigma_b = -\left(\frac{4\pi}{3}\right)([A]\chi_{M,A} + [B]\chi_{M,B}) \tag{6a}$$

$$\sigma_m = [A]\sigma^*_{m,A} + [B]\sigma^*_{m,B} \tag{6b}$$

of the components. For ideal solutions (in absence of excess volumes) or for dilute solutions, the molar concentrations are linearly correlated. This relationship can be expressed by eq 7, suitable for a solution of A in B, where $[B]° = 1/vB°$ is the

$$[B] = [B]° - \frac{vA}{vB°}[A] \tag{7}$$

molar concentration (density) of pure liquid B, and vA is the partial molar volume of component A in an infinitely dilute solution of A in B (for ideal solutions, vA is constant over the whole range of composition). The chemical shift of ^{129}Xe for these solutions should therefore depend linearly on [A] with a slope, $\partial\delta/\partial[A]$, given by eqs 8 where $n_{s,A}$ and $n_{s,B}$ are the number of sites of type "s" in the molecular species A and B, respectively.

$$\frac{\partial\delta}{\partial[A]} = -\left(\frac{\partial\sigma_b}{\partial[A]} + \frac{\partial\sigma_m}{\partial[A]}\right) \tag{8a}$$

$$\frac{\partial\sigma_b}{\partial[A]} = -\frac{4\pi}{3}\left(\chi_{M,A} - \frac{vA}{vB°}\chi_{M,B}\right) \tag{8b}$$

$$\frac{\partial\sigma_m}{\partial[A]} = \left(\sigma^*_{m,A} - \frac{vA}{vB°}\sigma^*_{m,B}\right) = \sum_s \left(n_{s,A} - \frac{vA}{vB°}n_{s,B}\right)\sigma^*_s \tag{8c}$$

Figure 3 displays the experimental data for a solution of lauric acid, $CH_3(CH_2)_{10}COOH$ (a solid at room temperature) in *n*-heptane. The ratio $vA/vB°$, obtained from the dependence of [heptane] on [lauric acid] using eq 7, is 1.53 ± 0.02. Assuming ideality of the lauric acid−heptane solution, the ratio $vA°/vB°$ is estimated to be 1.534. Indeed, the extrapolation of the molar volumes of *n*-alkyl acids with $4 \le n_C \le 8$ (derived from d^{20} values)[34] leads to an estimation of $vA°$ for pure *liquid* lauric acid at 20 °C of 224.8 cm^3 mol^{-1} and the density of pure liquid *n*-heptane gives $vB° = 146.55$ cm^3 mol^{-1}. Using the group contribution determined in the present study (Table 1), the molar magnetic susceptibility of *n*-heptane ($-85.38\ 10^{-6}$ mol^{-1} cm^3),[33] and a value of -148×10^{-6} mol^{-1} cm^3 for the molar magnetic susceptibility of lauric acid (estimated from linear extrapolation of χ_M values for $4 \le n_C \le 8$),[33] eq 8 give 4.4 ppm M^{-1} for the slope of the linear dependence of δ on [lauric acid]. This value is in excellent agreement with the experimental value, measured to be 4.38 ± 0.08 ppm M^{-1} (Figure 3). Its worth noting that $\partial\delta/\partial[A]$ is calculated from the difference between positive values which are large and similar ($-\sigma^*_{m,A}$ and $vA/vB° - \sigma^*_{m,B}$; see eq 8) and is therefore highly sensitive to imprecisions on $vA/vB°$.

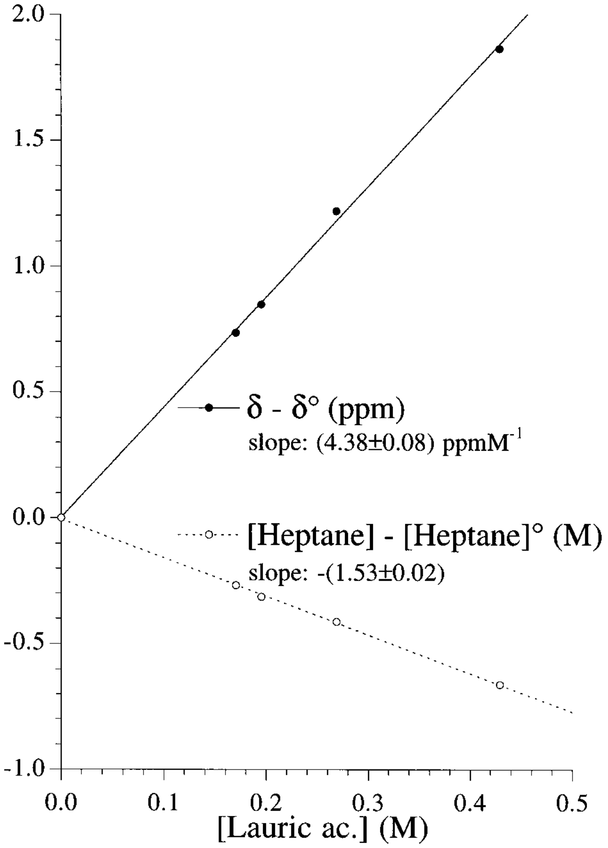

Figure 3. Filled points: difference between the ^{129}Xe gas-to-solution NMR chemical shifts at 293 K in dilute solutions of lauric acid in heptane (δ) and the value in pure heptane ($\delta°$). Open points: difference between the molar concentration of heptane in dilute solutions of lauric acid in heptane at 293 K ([heptane]) and the value in pure heptane ([heptane]°).

Discussion

Relative Contribution of Methyl and Methylene Groups in Linear Solvents. The deshielding effect due to methyl groups is found to be larger than the effect produced by methylene groups: $-\sigma^*_{CH_3} = 3.95$ ppm M^{-1} and $-\sigma^*_{CH_2} = 3.29$ ppm M^{-1}. This differs from results reported by Lim et al.[31] Since ^{129}Xe gas-to-solution NMR shifts are dominated by the decrease in shielding due to the van der Waals xenon−solvent interactions (σ_w) and since they have been shown to be directly proportional to the Xe−solvent London energy,[22] it is of interest to compare the relative amplitudes of the group contribution determined in the present work to Xe−CH$_3$ and Xe−CH$_2$ dispersive interaction energies. van der Waals interaction energies are frequently calculated using pairwise additive interaction potentials of the Lennard-Jones form (see eq 9a, where r is the distance between

$$U_{LJ} = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\} \tag{9a}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad \epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \tag{9b}$$

$$\langle U_{\mathrm{disp}} \rangle = -4\pi\rho \int_0^\infty \mathrm{d}r\, r^2 4\epsilon \left(\frac{\sigma}{r}\right)^6 g(r) \tag{10}$$

interaction sites). ϵ and σ parameters can be found in the literature: for Xe−Xe interactions $\epsilon = 0.5$ kcal/mol and $\sigma = 3.9$ Å,[37] for $CH_3{-}CH_3$ $\epsilon = 0.175$ kcal/mol and $\sigma = 3.905$ Å,[38] and for $CH_2{-}CH_2$ $\epsilon = 0.118$ kcal/mol and $\sigma = 3.905$ Å.[38] Interaction parameters between unlike groups, such as $Xe{-}CH_3$ and $Xe{-}CH_2$, are then calculated by means of the Lorentz−Berthelot combination rules (eq 9b).

For monoatomic species, the dispersive interaction energy is given by eq 10. In the gas phase, the radial distribution function $g(r) = e^{-U_{LJ}/kT}$, while in the liquid phase, it has been shown[39] that the use of a Heaviside step function ($g(r) = 0$ for $r < \sigma$ and 1 otherwise) leads to reliable estimates of internal energies. If the methyl and methylene groups are considered as independent single Lennard-Jones particles, eqs 9 and 10 and the interaction parameters found in the literature, give 1.26 and 1.22 for the ratio $\langle U_{\mathrm{disp,Xe-CH_3}}\rangle/\langle U_{\mathrm{disp,Xe-CH_2}}\rangle$ in the gas and liquid phases, respectively. In linear solvents, the ratio of the molar deshielding effect due to methyl groups to the effect of methylene groups is $-\sigma^*_{CH_3}/-\sigma^*_{CH_2} = 1.20$; the good agreement between this value and the estimates of the relative $Xe{-}CH_3$ and $Xe{-}CH_2$ dispersive interaction energies validates the present group contribution analysis of the ^{129}Xe gas-to-solution NMR shifts.

Contribution of Methylene Groups in Linear and Cyclic Alkanes. The group contributions, $-\sigma^*_s$, which are obtained from the experimental $-\sigma^*_m$ values, are ensemble averages and thus depend on the distribution of the particular group around the Xe atom (see eq 4). This means that a single Xe−group intermolecular shielding function, for example the $Xe{-}CH_2$ function, can lead to different $-\sigma^*_{CH_2}$ values in various solvents, or even for different methylene groups in the same solvent molecule, if the local arrangement of the various $-CH_2-$ group around the Xe atom are different.

In linear solvents, the same $-\sigma^*_{CH_2}$ value is found for the various series. It is unlikely that for each series compensations occur between the $Xe{-}CH_2$ shielding functions and the distributions of $-CH_2-$ groups around the Xe atom; a single $Xe{-}CH_2$ shielding function and very similar $-CH_2-$ group distributions are more easily conceivable. A search for *effective* transferable shielding functions, along the same line of ideas adopted for intermolecular potential functions, is therefore pertinent.

In cycloalkanes, the value for $-\sigma^*_{CH_2}$ is found to be significantly smaller than the value characterizing the linear solvents. No reasonable physical argument can be put forward to justify a search for a specific $Xe{-}CH_2$ shielding function for cyclic solvents. Moreover, the fact that the same intermolecular van der Waals interaction potentials are used for CH_2 in linear and cyclic alkanes[38] is consistent with the idea of a single $Xe{-}CH_2$ shielding function. Therefore, in our opinion the fact that different $-\sigma^*_{CH_2}$ values are found for cycloalkanes and *n*-alkanes reflects differences in the arrangement of $-CH_2-$ groups around the Xe atom. This is probably a consequence of the additional geometric constraints imposed by the cyclic molecular structure. It is clear that the approximation of monoatomic species used here, i.e., that the building groups behave independently, is better for solvent molecules for which the internal degrees of freedom allow the sampling of multiple conformations. For instance, the diversity of stable molecular conformations is smaller for cyclohexane than for *n*-hexane and, furthermore, the chair inversion process is a rare event with respect to the residence time of a xenon atom close to a particular cyclohexane molecule. The Xe atom therefore *sees* the cyclohexane molecule as a rigid molecule (vibrations are rapid with respect to the diffusion) and the geometry of the rigid molecule should therefore be reflected in the distribution of $-CH_2-$ groups around the Xe atom. This has been observed in the case of the Xe−C pair distribution function obtained by MD simulations for xenon in benzene.[24] It would be of interest to make use of computer simulation techniques in order to confirm that a single $Xe{-}CH_2$ shielding function is able to reproduce the experimental $-\sigma^*_{CH_2}$ value in both cyclic and linear alkanes. Finally, in the previous section we pointed out that the quality of the linear adjustment of $-\sigma^*_m$ versus n_C is not as good for cycloalkanes as for the set of linear solvents. This is not surprising since it is known that, for increasing ring size, nonregular trends are observed for various properties of cycloalkanes (for instance, the heat of combustion per number of methylene groups).[40] Eight- to twelve-membered rings exhibit peculiar physical and chemical properties and the characteristics of cycloalkanes slowly converge to those of the corresponding linear alkanes. Even though such a convergence must occur for the ^{129}Xe medium NMR shift, it is not expected for short to medium rings (see Figure 2).

^{129}Xe Gas-to-Solution NMR Shifts in the Short-Chain Solvents. We observed that the chemical shift in the shortest members of the series deviate from the general trend dictated by the long-chain solvents. These deviations are in part due to density effects. Indeed, the ^{129}Xe chemical shifts are larger in acetone and in acetic acid than in diethyl ketone and propanoic acid respectively; the molar medium effects, $-\sigma^*_m$, on the other hand are smaller (see Figures 1 and 2). The remaining deviation could result from distinctive intramolecular or intermolecular features of the short-chain solvents that affect either the local distribution of sites around the Xe atom and/or the Xe−site shielding functions. In the case of acetone where the remaining deviation is quite large, the intramolecular and intermolecular features that need to be taken into consideration are (i) the *fixed* distance between both methyl groups, (ii) the fact that the methyl groups adjacent to a carbonyl function are not equivalent to a methyl group next to a methylene, (iii) the importance of solvent−solvent electrostatic interactions, and (iv) the importance of many-body effects. The geometrical constraint mentioned in (i) might affect the $Xe{-}CH_3$ pair distribution function in a manner similar to the way the ring affects the $Xe{-}CH_2$ distribution function in cyclic alkanes. The nonequivalence mentioned in (ii) implies that a specific $Xe{-}CH_3$ shielding function might have to be defined. In pure acetone, the electrostatic interactions contribute for more than 30% to the total interaction energy[30] (point iii), and they are likely to influence the arrangement of the solvent molecules around a (hydrophobic) solute such as xenon. As far as many-body effects are concerned, it is worth reminding that in addition to the deshielding effect due to van der Waals interaction (σ_w), fluctuating electric fields of electrostatic origin can affect the screening constant of a nucleus (the σ_{e2} term; eq 1b). For Xe interacting with a polar group such as the carbonyl function, the measured $-\sigma^*_s$ value is the sum of the σ^*_w and σ^*_{e2} contributions. The latter is not expected to be additive: i.e., the fluctuation of the total electric field experienced by the xenon atom is not equal to the sum of the field fluctuations due to each polar group. Group contributions derived from long-chain solvents, in which the polar function is “diluted” into the nonpolar groups, might then be inadequate for short alkyl chain solvents. Changes in the structure of the xenon solvation shell,

as considered in point (iii), are liable to influence strongly the σ^*_{e2} contribution. It is worth noting that similar considerations are valid as far as electric fields originating from the induced electric moments of the solvent molecules are concerned and, finally, that the van der Waals contribution (σ^*_w) might also be affected by solvent−solvent interactions.

Mixtures of acetone and *n*-alkanes were considered by Stengle and co-workers.[20] They observed that the addition of small amounts of acetone to *n*-heptane moves the ^{129}Xe chemical shift, δ, upfield with respect to the value in pure liquid *n*-heptane even though δ in pure acetone (173 ppm) is approximately 10 ppm downfield. The authors estimated the chemical shift of ^{129}Xe dissolved in *hypothetical* "free molecular acetone" to be 161 ± 2 ppm (at 25 °C); much the same value is obtained regardless of which alkane is used as a cosolvent. The experimental observation of different deshielding medium effect caused by acetone molecules at infinite dilution in *n*-alkanes and in pure liquid acetone is most probably a consequence of acetone−acetone interactions in the xenon solvation shell. The relative importance the effects described in point (iii) and (iv) cannot be a priori estimated. Here again, computer simulations could help in investigating their relative importance.

Conclusions

The success of a group contribution analysis in interpreting medium effects requires additivity of the intermolecular interactions responsible for these effects. This condition is generally fulfilled for ^{129}Xe gas-to-solution NMR chemical shifts since they are dominated by the shielding due to van der Waals Xe−solvent interactions. The present paper demonstrates that when the solvent density is taken into account, a meaningful group contribution analysis of the ^{129}Xe gas-to-solution chemical shift is possible. These contributions can be tested against computer simulation results and used to build a library of transferable intermolecular shielding functions in a manner similar to the approach adopted in the determination of effective intermolecular potential functions.

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Supporting Information Available: Tables of data related to the *n*-alkane, cycloalkane, *n*-alkyl alcohol, *n*-alkyl acid, and ketone series of solvents (7 pages). Ordering information is given on any current masthead page.

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