alkali metal cations Li^+, Na^+, and K^+ in propylene carbonate solvent. They also reported values of free energies of transfer of these ions from water to propylene carbonate. From a plot similar to Figure 7 they estimated that between two and three water molecules were involved in specifically solvating the alkali metal ions. If all the changes in the "solvent activity coefficients" and in the ion–ligand displacement constants in Figure 7 are attributed to specific ion–polar molecule interaction at short range, then the slopes we calculated above imply that one to two molecules of the solvents are involved in the "transfer process" represented by the "solvent activity coefficients." Of course, a more meaningful comparison could be made if cation–ligand association constants were available for these ligands we consider here interacting with Na^+ or Li^+ in a relatively inert solvent. This is an area of research being pursued in this laboratory.

In conclusion, the process involved in specific interaction between tertiary ammonium ions and Lewis bases at short range in solution has been shown to be very similar to that involved in the interaction of alkali metal cations and the molecules of solvent in a number of polar solvents and also to that involved in the formation of hydrogen-bonded complexes between the Lewis bases and *p*-fluorophenol in CCl_4 solvent. Recall that the first and the last of the three processes above do not correlate with measures of proton basicity in the Brønsted sense. It follows then that there is a greater similarity of the energetics of the process of hydrogen-bond formation to the energetics of specific cation–Lewis base interaction than to the energetics of proton-transfer processes.

Supplementary Material Available. Conductance data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-8551.

Absolute Temperature Dependence of Chemical Shifts of Lock Solvents. Tetramethylsilane, Hexafluorobenzene, and 1,4-Dibromotetrafluorobenzene

A. Keith Jameson*[1a] **and Cynthia J. Jameson**[1b]

Contribution from the Departments of Chemistry, Loyola University, Chicago, Illinois, and University of Illinois at Chicago Circle, Chicago, Illinois 60680.

Received April 7, 1973

Abstract: Temperature-dependent studies in nmr have heretofore suffered from the unknown temperature dependence of the reference substance. We have measured the ^{129}Xe resonance frequency in Xe gas extrapolated to zero density using three external references (^1H in TMS and ^{19}F in C_6F_6 and DBTFB) over the range 240 to 440°K. Because of the nature of the isolated xenon atom it should have a rigorously temperature-independent chemical shielding. Hence, the measured temperature dependence is due solely to the external references used. The experimental temperature dependence of chemical shifts for TMS, C_6F_6, and *p*-$C_6Br_2F_4$ reported here provides convenient external references for temperature-dependent studies over the range 240 to 440°K.

In nmr spectroscopic measurements at variable temperatures, the lock solvent or reference substance with respect to which shifts are being measured is itself changing with temperature. This change is generally neglected. Depending on the magnitude of the shifts being measured relative to the magnitude of the reference substance shifts, this could lead to large or small errors in the temperature dependence of interest. The problem is that it is difficult to keep the reference substance at some fixed constant temperature while varying the temperature of the sample. In the use of an internal reference there are two problems. (1) The reference substance would be changing in temperature along with the sample under study. Also, (2) interactions between the reference substance and the sample are very likely temperature dependent. Use of an external reference in a sealed capillary tube or in the outer or inner annular region of coaxial sample tubes eliminates the second problem but not the first.

The temperature-dependent chemical shifts in gases reported by Petrakis and Sederholm were measured relative to CH_4 which was mixed in nearly equimolar amounts with the gases under study.[2] These reported shifts include the intrinsic temperature dependence of methane (temperature dependence of an isolated CH_4 molecule being used as reference) as well as the temperature dependence of the CH_4–CH_4 and CH_4–sample intermolecular interactions. The latter might be negligible since the densities used were quite small (about 5 amagats of each). Even so, one would still need an absolute measure of the CH_4 temperature dependence (due to change in vibrational and rotational averages of chemical shielding with temperature)[3] in order to find the real temperature dependence of the gases of interest. Similarly, Widenlocher measured the temperature dependence of H_2S relative to C_2H_6, HCl, and $(CH_3)_2O$ and CH_3Cl relative to CH_4 in mixtures of

---

(1) (a) Loyola University; (b) University of Illinois.

(2) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1174 (1961).

(3) A. D. Buckingham, *J. Chem. Phys.*, **36**, 3096 (1962).

roughly 5 amagats of each gas with 5 amagats of the reference.[4] He reported nonlinear curves of relative frequency with temperature for most of the gases over an 80° range. However, like the data of Petrakis and Sederholm, these curves are difference curves (that is, the difference between the intrinsic temperature dependence of the sample and that of CH_4 or C_2H_6). Rummens, Raynes, and Bernstein[5] reported shifts of various liquids using as a reference acetone in a capillary inside the sample tube with the neat liquid. Here again, the temperature dependence is assumed to be linear over the range of temperatures studied (range varies from 55 to 165°) and measured relative to the acetone ^1H signal which is itself temperature dependent. In both the Petrakis and Sederholm data and the Rummens, Raynes, and Bernstein data, the reported relative T dependence of 18 various gases and liquids is very small, of the order of (0 to 2) $\times 10^{-4}$ ppm/deg. This is not surprising. If the reference signal were shifting with T in the same direction as the gas or liquid of interest, then only very small relative changes can be observed.

Meinzer tried the following method of obtaining absolute temperature dependence of various liquids and gases.[6] A melting point capillary tube containing the reference was placed in the probe outside the dewar jacket but inside the Faraday shield so that the reference substance nominally remained at room temperature while the sample temperature was varied. A small external coil of 12 tightly wound turns of enameled copper wire was wrapped around the capillary tube. The coil was connected to the radiofrequency transmitter *via* a simple circuit. A thermocouple was placed near the capillary tube and the temperature was found to remain constant while the sample temperature was varied. A difficulty encountered was that the frequency of the signal from the capillary could be changed almost 70 Hz by changing its position. Thus, special care had to be taken that the capillary not be misaligned while taking spectra over a temperature range.

Most reports of temperature dependence also suffer from the assumption that the change in resonance frequency is linear with temperature. Thus, a single number is reported, the slope of this assumed linear dependence. However, this may be valid only over a very narrow temperature range. There is no *a priori* reason to believe that shifts with temperature should be linear.

We have determined the absolute temperature dependence of three commonly used lock substances as a by-product of our studies on the temperature and density dependence of ^{129}Xe chemical shifts in xenon gas. The lock substances used were the following: tetramethylsilane (240 to 300°K), hexafluorobenzene (280 to 340°K), dibromohexafluorobenzene (350 to 440°K).

Several xenon samples of densities ranging from 19 to 122 amagats were prepared by the method previously described.[7] These samples of xenon in sealed thick-walled glass tubes fit into the standard thin-walled 5-mm o.d. nmr tubes with enough annular space for the lock substance. The sample tubes were about 5 cm long. This short length was necessary in order that the entire sample could be maintained within the constant temperature region in the dewar insert. Different lock substances were used in order to cover a wide temperature range. The ^{129}Xe signal was observed with a Bruker HFX90 spectrometer with a 21 kG high-resolution magnet. Signal accumulation was accomplished over 2 to 64 scans. Temperature regulation was carried out, with nitrogen as the heat exchange gas, by a digital unit with a three-decade digital indicator to set the temperature and a meter to indicate the deviations from this setting. The regulator was calibrated at the ice point and the linearity of the regulator reading with temperature was checked with a sample of methanol (CH_3 relative to OH shift) in the proton probe insert with the field locked to TMS. The absolute temperature readings in the xenon probe insert were calibrated at the boiling points of TMS and C_6F_6 and the freezing point of C_6F_6. The absolute temperatures were probably accurate to ± 1° and the precision was about ±0.2°.

Since the xenon molecule has no vibrational or rotational degrees of freedom and no low-lying electronic states, the only possible source of temperature dependence is the intermolecular interaction between Xe molecules. When the xenon resonance frequency is measured at various temperatures for samples of known densities with the field locked to the signal of the lock substance, the data can be extrapolated to zero density at each temperature. The frequency at the limit of zero density at each temperature is the resonance frequency of ^{129}Xe in the isolated xenon atom. Since the isolated xenon atom should have no temperature dependence, then any apparent temperature dependence in the ^{129}Xe frequencies is due to the temperature dependence of the lock substance. The xenon frequency is fitted to a second-degree polynomial in T for each sample of a given density. The coefficients of the zeroth-order term, $a_0(\rho)$, first-order term, $a_1(\rho)$, and second-order term, $a_2(\rho)$, in temperature for each sample of given density are then plotted as a function of density. The intercepts (at zero density) give the temperature coefficients of the lock substance itself.

The absolute temperature dependencies of ^1H chemical shielding in TMS and of ^{19}F in C_6F_6 and in dibromotetrafluorobenzene are given below, where $t_0 = 300$°K

$$\nu = a_0^{(0)} + a_1^{(0)}(T - t_0) + a_2^{(0)}(T - t_0)^2$$

for TMS and C_6F_6 and 350°K for dibromotetrafluorobenzene. $a_0^{(0)}$ just gives the resonance frequency of an isolated Xe atom at t_0 when the field is locked to the signal of the specific lock substance and is of no interest insofar as the lock substance temperature dependence is concerned. The superscripts (0) refer to zero density and the subscripts refer to the power to which the temperature is raised.

$$\text{TMS:}\quad a_1^{(0)} = (+0.378 \pm 0.251) \times 10^{-2}\ \text{ppm/°K}$$

$$a_2^{(0)} = (-0.197 \pm 0.034) \times 10^{-3}\ \text{ppm/°K}^2$$

$$C_6F_6\text{:}\quad a_1^{(0)} = (+0.115 \pm 0.021) \times 10^{-1}\ \text{ppm/°K}$$

$$a_2^{(0)} = (-0.207 \pm 0.036) \times 10^{-3}\ \text{ppm/°K}^2$$

$$\text{DBTFB:}\quad a_1^{(0)} = (-0.350 \pm 0.365) \times 10^{-2}\ \text{ppm/°K}$$

$$a_2^{(0)} = (+0.372 \pm 0.009) \times 10^{-4}\ \text{ppm/°K}^2$$

---

(4) G. Widenlocher, *Ann. Phys. (Paris)*, 1, 327 (1966).

(5) F. H. A. Rummens, W. T. Raynes, and H. J. Bernstein, *J. Phys. Chem.*, 72, 2111 (1968).

(6) R. A. Meinzer, Ph.D. Thesis, University of Illinois, 1965.

(7) A. K. Jameson, C. J. Jameson, and H. S. Gutowsky, *J. Chem. Phys.*, 53, 2310 (1970).

The functions

$$\nu = a_0^{(0)} + a_1^{(0)}(T - t_0) + a_2^{(0)}(T - t_0)^2$$

are plotted in Figure 1. They show that the temperature dependence is not representable by a straight line over the entire range. Thus, the assumption of a linear function of temperature by other workers is probably unjustified. Since there are standard deviations associated with the $a_1^{(0)}$ and $a_2^{(0)}$ values, as given above, the exact temperature at which minima or maxima occur, or even the definite presence of such extrema, should be considered with these standard deviations in mind.

Our data may be compared with those obtained by Meinzer by the external capillary method for the following liquids from 0 to 30 or 40°.[6] They are the same

^{1}H in CH_3Cl	0.472×10^{-2} ppm/deg	0 to 30°
^{1}H in acetone	0.33×10^{-2} ppm/deg	0 to 30°
^1H_3C in CH_3OH	0.271×10^{-2} ppm/deg	0 to 40°

order of magnitude as the shifts we have observed for TMS, C_6F_6, and DBTFB, and if we limit the range of temperature to about 30 deg, the curves would appear to be linear. The data of Petrakis and Sederholm[2] cannot be compared with ours. They report for TMS a shift with temperature of -2.08×10^{-4} ppm/deg relative to CH_4 taken as zero. However, CH_4 itself should have a finite shift with temperature. The very small relative shift they report for TMS indicates that CH_4 has a shift in temperature much like that of TMS.

We used a coaxial arrangement, the inner tube containing the sample, the annular region the lock substance. Since the geometry is not spherical, there are obviously bulk susceptibility contributions to the chemical shielding. We can be confident that there are no significant environmental differences between sample and annular regions; with TMS in both regions we obtained a single peak when the sample tube was spinning, with no observable "wiggle-beat" in the ringing pattern. This was over the temperature range 240–300°K. Hence, the environments in the annular and sample regions were identical to well within 1 Hz insofar as observed chemical shift is concerned. There is, however, the temperature dependence of the bulk susceptibility which still remains. Hence, the values of $a_1^{(0)}$ and $a_2^{(0)}$ as given contain this very slight temperature dependence of the bulk susceptibility.

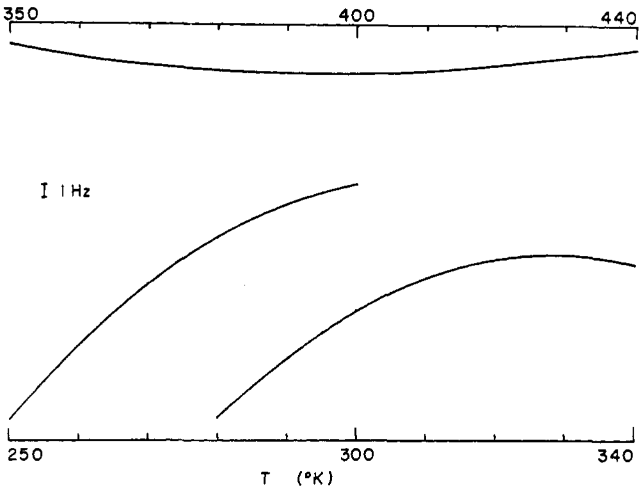

Figure 1. Absolute temperature dependence of ^{1}H chemical shift in tetramethylsilane (at 250–300°K), and ^{19}F chemical shift in hexafluorobenzene (280–340°K) and 1,4-dibromotetrafluorobenzene (350–440°K).

The temperature dependencies we report here for three lock substances show nonlinear behavior over a wide temperature range and are absolute temperature shifts, since they are in effect taken relative to an isolated xenon atom, which has a temperature-independent chemical shielding due to lack of intermolecular interactions and lack of internal degrees of freedom. Temperature-dependence measurements on other systems can now easily be made by using any of the three reference substances whose temperature dependence we report here. Since the temperature dependence of the solvents given here contains the temperature dependence of the bulk susceptibility, then by adopting the same geometry as we used, other workers can determine the temperature dependence of their own systems by subtracting out the temperature dependence of the external references given here. Of course the temperature dependence of the bulk susceptibility of their own chemical system still remains.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation (GP-29719).