A Study of Dielectric Solvent Effect on Silicon-29 NMR Chemical Shifts of Some Chlorosilanes

Toshio TAKAYAMA,* Isao ANDO,† and Tetsuo ASAKURA††
Department of Applied Chemistry, Faculty of Technology, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221
†Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
††Department of Biopolymer Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Nakamachi 2-chome, Koganei, Tokyo 184
(Received October 8, 1988)

The dielectric solvent effect on the ^{29}Si NMR chemical shifts of some chlorosilanes is calculated by means of the finite perturbation theory within the CNDO/2 framework using the solvaton theory which is employed to estimate specific solute-solvent bonded interactions as a function of the dielectric constant of the medium. The calculated variations are reasonably compared with the gross trend of the observed solvent effects of ^{29}Si chemical shifts. Further, the origin of the dielectric solvent effect is discussed.

Chemical shift in NMR is known to be solvent dependent. ^{13}C NMR chemical shifts in various solvents have been observed and have been well-interpreted theoretically by means of the "solvaton"-MO theory.[1] The polar effects of aprotic solvents on nuclear shielding may be accounted for by means of an imaginary particle called the "solvaton" model.[2-4] This has been successfully employed in the calculation of solvent effects on ^{13}C chemical shifts in a number of molecules.[5-7] According to our best knowledge, there is little systematic calculation by sophisticated methods of solvent effect on ^{29}Si chemical shift considered here.

Therefore, the above approach can be extended to ^{29}Si chemical shifts of some organic compounds containing silicon atom.[8] The purpose of this work is to measure the ^{29}Si NMR chemical shifts of chlorosilanes in various kinds of solvents over a wide range of dielectric constants. Further, we aim to study theoretically dielectric solvent effects on ^{29}Si chemical shifts of chlorosilanes by the finite perturbation theory (FPT)[6] within the CNDO/2 framework.[9] For this, the solvaton model has been employed to study the effect of solvation on the screening of this nucleus in aprotic solvents. It is anticipated that its model may provide a substantial insight into the effects of solute-solvent interactions on the experimentally observed chemical shifts.

Theoretical

For convenience, we describe briefly the "solvaton" theory. In this theory it is assumed that (1) a number of charges (the "solvaton") are induced in the solvent when a solute is infinitely diluted with an aprotic solvent of dielectric constant, ε; and (2) one solvaton is associated with each atomic center of the solute molecule and its charge is equal in magnitude but opposite in sign; and (3) there are no interactions between them. From these assumptions it follows that the strength of the interaction between the solute and the "solvaton" depends on the polar nature of the solvent. The Hamiltonian, H, of the specified molecular system with M electrons and N nuclei consists of the inherent term, H_{inh}, and the solvent interaction term, H_{solv}, and is given as (in atomic units)

$$H = H_{\text{inh}} + H_{\text{solv}}, \tag{1}$$

where

$$H_{\text{inh}} = \sum_{i=1}^{M}\left[-\frac{1}{2}\nabla_i^2 - \sum_{n=1}^{N}\frac{Z_n}{r_{ni}}\right] + \frac{1}{2}\sum_{i}^{M}\sum_{j}^{M}\frac{1}{r_{ij}} + \frac{1}{2}\sum_{k}^{N}\sum_{l}^{N}\frac{Z_k Z_l}{r_{kl}}, \tag{2}$$

$$H_{\text{solv}} = \frac{(\varepsilon-1)}{2\varepsilon}\left[\sum_{i}^{M}\sum_{s}^{N}\frac{Q_s}{r_{si}} - \sum_{k}^{N}\sum_{s}^{N}\frac{Q_s Z_k}{r_{sk}}\right], \tag{3}$$

in which Q_s is the induced "solvaton" charge, r_{si} and r_{sk} are the "solvaton"-electron and "solvaton"-nucleus distances respectively, and Z_i is the nuclear charge. The first term in Eq. 3 is the interaction energy of the electrons and the induced solvent charges while the last term represents the interaction energy between the induced solvent charges (solvaton) and the nuclear core charges. The function of the solvent dielectric constant, $(\varepsilon-1)/2\varepsilon$ determines the degree of solvent-solute interaction. In these calculations, if the AO's and "solvaton" are associated with the same atomic center as the "solvaton"-electron distance r_{si}, the van der Waals radius of the particular atom type is used and if the AO's and "solvaton" are associated with different atomic centers, the "solvaton" is assumed to be centered on the atomic center associated with S and then r_{si} is evaluated. The solvent interaction was incorporated into the FPT-CNDO/2 method proposed by Pople et al.[9,10] As the effective van der Waals radius of silicon atom, 2.00 Å is used.[11] The detail of the calculation is described elsewhere.[1,4]

In this calculation, values used for bond lengths were 2.01, 1.87, 1.48, and 1.09 Å for the Si-Cl, Si-C,

Si-H, and C-H, respectively, and all the ∠C-Si-Cl, ∠Cl-Si-Cl, ∠H-Si-Cl, and ∠Si-C-H bond angles were set at 109.47°.[12] All calculations were carried out by means of a FACOM VP-30 computer at the Computer Center of Kanagawa University, a HITAC M-280H computer of the Tokyo Institute of Technology, and a HITAC S810 computer at the Institute for Molecular Science, Okazaki.

Experimental

All of chlorosilanes, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, $(CH_3)SiCl_3$, $(CH_3)_2HSiCl$, $(CH_3)HSiCl_2$, $HSiCl_3$, and $SiCl_4$ were commercially available spectral-grade products. Solvents used were dried under usual precautions and distilled under an atmosphere of nitrogen: Hexane (ε=1.9), carbon tetrachloride (ε=2.23), chloroform (ε=4.6), tetrahydrofuran (ε=7.39), and acetone (ε=20.7), where the value of the dielectric constant at 20 °C is indicated in parenthesis.[13]

The ^{29}Si NMR spectra were measured by means of a JEOL FX90Q spectrometer operating at 17.75 MHz equipped with a Fourier transform accessory. The measurements were made using the 20% (v/v) solutions of the above-mentioned solvents for chlorosilanes at the probe temperature of 22.4 °C in a 10 mm o.d. NMR tube, and deuterated benzene and tetramethylsilane sealed off in a 5 mm o.d. capillary were used as ^2D lock and an external reference. The observed free-induction decay after a 45° pulse width of 7.0 μs was sampled in 8192 data points and the pulse recycle time was 20 s. The ^{29}Si chemical shift was corrected for bulk magnetic susceptibility.[14] The bulk magnetic susceptibility for a solution, X_{soln}, is given as

$$X_{soln} = \sum_i^n \phi_i X_i, \quad (4)$$

where ϕ_i and X_i are the volume fraction and the bulk magnetic susceptibity of the i-th component molecule in solution, respectively.

Results and Discussion

Observed dielectric solvent effect of NMR chemical shift: The observed ^{29}Si chemical shifts of chlorosilanes in various solvents are plotted as a function of $(\varepsilon-1)/2\varepsilon$ in Fig. 1.

The factor $(\varepsilon-1)/2\varepsilon$ was chosen as abscissa because the chemical shielding is found to be proportional to $(\varepsilon-1)/2\varepsilon$ as described previously.[1] $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, $(CH_3)SiCl_3$, $(CH_3)_2HSiCl$, $(CH_3)HSiCl_2$, and $HSiCl_3$ chlorosilanes show linearly downfield shift with increasing $(\varepsilon-1)/2\varepsilon$, but the chemical shift of $SiCl_4$ is almost independent of ε. This indicates that ^{29}Si chemical shift is linearly proportional to $(\varepsilon-1)/2\varepsilon$ as well as in the case of ^{13}C chemical shift. The observed ^{29}Si shifts for chlorosilanes can be fitted approximately by

$$\delta = A\left(\frac{\varepsilon-1}{2\varepsilon}\right) + B. \quad (5)$$

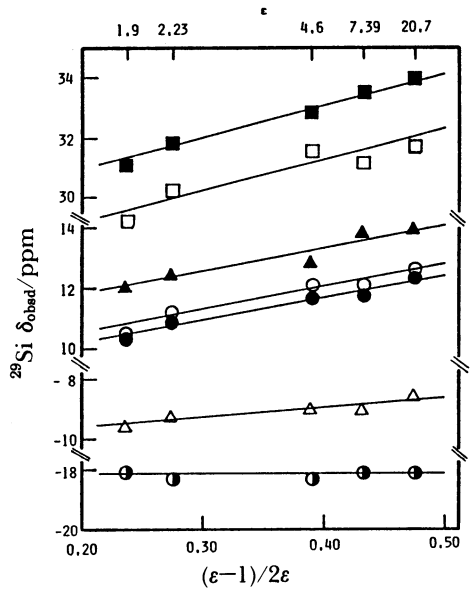

Fig. 1. Dependence on dielectric constant e of the observed ^{29}Si NMR chemical shifts δ in chlorosilanes. The positive sign means downfield shift. The sysmbols used refer to the following compounds: $(CH_3)_2SiCl_2$ (■),$(CH_3)_3SiCl$ (□), $(CH_3)SiCl_3$ (▲), $(CH_3)_2HSiCl$ (○),$(CH_3)HSiCl_2$ (●), $HSiCl_3$ (△), $SiCl_4$ (◑). The straight line was obtained by the linear least-squares fitting.

Table 1. The Variation of the Observed ^{29}Si Chemiccal Shift in Chlorosilanes as in Going from ε=1.9 to 20.7

Compound	Parameter/ppm[b]			
	$\Delta\delta_{obsd}$/ppm[a]	A_{obsd}	B_{obsd}	r[c]
$(CH_3)_3SiCl$	2.3	9.8	27.2	0.93
$(CH_3)_2SiCl_2$	2.8	11.8	28.3	0.99
$(CH_3)SiCl_3$	1.9	7.7	10.2	0.96
$(CH_3)_2HSiCl$	1.9	8.0	8.8	0.97
$(CH_3)HSiCl_2$	1.8	7.8	8.6	0.99
$HSiCl_3$	0.8	3.4	−10.4	0.91
$SiCl_4$	ca. 0	ca. 0	−18.2	0.2

a) $\Delta\delta_{obsd}=\delta_{obsd}(\varepsilon=20.7)-\delta_{obsd}(\varepsilon=1.9)$. A valus of δ_{obsd} corresponds to the linear least-squares fitting. The positive sign means downfild shift. b) The parameters are given by $\delta_{obsd}=A((\varepsilon-1)/2\varepsilon)+B$. c) Correlation coefficient.

The observed data fall approximately on a straight line plot of δ against $(\varepsilon-1)/2\varepsilon$. The magnitude of A provides a measure of the solvent effect on δ, whereas B is the value of δ in an isolated molecule. The parameters A and B can be obtained from the linear least-squares fitting. The variation of the observed ^{29}Si chemical shift ($\Delta\delta_{obsd}$) and the estimated values of parameters A_{obsd} and B_{obsd} for chlorosilanes in going from ε=1.9 to 20.7 are summarized in Table 1.

As seen from Table 1, the ^{29}Si chemical shifts of these compounds give an excellent correlation coefficient except for $SiCl_4$. The value of A_{obsd} for ^{29}Si nucleus is positive except for $SiCl_4$. This means that

the trend of the solvent effect is downfield shift. The observed chemical shift values cover a range from 0 ppm to 2.8 ppm with respect to hexane (ε=1.9).

Calculated dielectric solvent effect: Let us discuss the ^{29}Si chemical shift in chlorosilanes calculated as a function of ε by the CNDO/2 MO method using the "solvaton" theory. The results of the calculation of electron density (d), screening constants (σ^d, σ^P, and $\sigma^T(=\sigma^d+\sigma^P)$), chemical shift difference ($\Delta\sigma_{calcd}$), and correlation parameter (A_{calcd}) as a function of dielectric constant, are presented in Table 2.

Note that the calculated chemical shift (σ) is a nuclear shielding constant and so the negative sign means deshielding. On the other hand, the negative sign of the observed chemical shift (δ) means shielding. Therefore, the relative difference in the calculated chemical shift should be compared with the observed chemical shift. As seen from Table 2, the diamagnetic term, σ^d, moves slightly up-field in going from ε=1.0 to 20.7 for all compounds. This variation is consider-

Table 2. Dependences of the Calculated ^{29}Si Chemical Shifts and Correlation Parameters of Chlorosilanes and Electron Density on the Silicon Atom upon Dielectric Constant

	ε[a]	d	^{29}Si chemical shift/ppm				Parameter/ppm
			σ^d	σ^P	σ^T[b]	$\Delta\sigma_{calcd}$[c]	A_{calcd}[d]
$(CH_3)_3SiCl$	1.0	3.5475	68.01	−368.72	−300.70	−2.00	
	1.9	3.5733	68.36	−371.06	−302.70	0.0	
	2.23	3.5771	68.42	−371.40	−302.99	0.29	7.03
	4.6	3.5881	68.57	−372.37	−303.81	1.11	
	7.39	3.5919	68.62	−372.71	−304.09	1.39	
	20.7	3.5958	68.67	−373.05	−304.38	1.68	
$(CH_3)_2SiCl_2$	1.0	3.5519	68.07	−375.76	−307.69	−1.76	
	1.9	3.5822	68.49	−377.93	−309.45	0.0	
	2.23	3.5867	68.55	−378.22	−309.67	0.22	5.56
	4.6	3.5995	68.72	−379.05	−310.33	0.88	
	7.39	3.6038	68.78	−379.33	−310.55	1.10	
	20.7	3.6082	68.84	−379.62	−310.78	1.33	
$(CH_3)SiCl_3$	1.0	3.5556	68.12	−382.64	−314.51	−1.55	
	1.9	3.5917	68.61	−384.68	−316.06	0.0	
	2.23	3.5970	68.69	−384.95	−316.27	0.21	4.73
	4.6	3.6120	68.89	−385.71	−316.82	0.76	
	7.39	3.6170	68.96	−385.96	−317.00	0.94	
	20.7	3.6222	69.02	−386.22	−317.19	1.13	
$(CH_3)_2HSiCl$	1.0	3.5539	68.10	−364.73	−296.63	−2.47	
	1.9	3.5767	68.41	−367.52	−299.10	0.0	
	2.23	3.5803	68.46	−367.92	−299.46	0.36	8.95
	4.6	3.5904	68.60	−369.11	−300.51	1.41	
	7.39	3.5938	68.64	−369.51	−300.87	1.77	
	20.7	3.5974	68.69	−369.93	−301.24	2.14	
$(CH_3)HSiCl_2$	1.0	3.5496	68.04	−369.29	−301.25	−2.17	
	1.9	3.5786	68.44	−371.86	−303.42	0.0	
	2.23	3.5830	68.50	−372.25	−303.76	0.34	7.70
	4.6	3.5955	68.67	−373.31	−304.65	1.23	
	7.39	3.5998	68.72	−373.67	−304.95	1.53	
	20.7	3.6042	68.78	−374.04	−305.26	1.84	
$HSiCl_3$	1.0	3.5453	67.98	−374.67	−306.69	−2.21	
	1.9	3.5823	68.49	−377.39	−308.90	0.0	
	2.23	3.5878	68.56	−377.77	−309.21	0.31	7.03
	4.6	3.6034	68.77	−378.80	−310.03	1.13	
	7.39	3.6086	68.84	−379.15	−310.30	1.40	
	20.7	3.6141	68.92	−379.50	−310.58	1.68	
$SiCl_4$	1.0	3.5573	68.15	−390.78	−322.64	−1.47	
	1.9	3.6009	68.74	−392.85	−324.11	0.0	
	2.23	3.6073	68.82	−393.09	−324.27	0.16	3.77
	4.6	3.6251	69.06	−393.79	−324.72	0.61	
	7.39	3.6310	69.14	−394.01	−324.87	0.76	
	20.7	3.6371	69.22	−394.23	−325.01	0.90	

a) Dielectric constants are employed (20 °C): Isolated molecule (ε=1.0), hexane (ε=1.9), carbon tetrachloride (ε=2.23), chloroform (ε=4.6), tetrahydrofuran (ε=7.39), and acetone (ε=20.7). b) $\sigma^T=\sigma^d+\sigma^P$. c) Calculated chemical shifts converted to the hexane scale. The positive sign means downfield shift. d) The parameter is given by $\sigma^T=A((\varepsilon-1)/2\varepsilon)+B$.

ably small. On the other hand, the paramagnetic term, σ^P, moves linearly downfield in going from ε=1.0 to 20.7. This means that the solvent effect of the ^{29}Si chemical shift is predominantly governed by the variation of the paramagnetic term.

It would be interesting to compare these calculated value with some observed data. The same relationship (Eq. 5) as the case of the observed data is also found in the calculated data. This agreement implies that there are no specific interactions between chlorosilanes and solvent molecules. This table has two features for the calculated solvent-induced shifts. First, we discuss the solvent-induced ^{29}Si chemical shift variations of $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, $(CH_3)SiCl_3$, and $SiCl_4$ series. The magnitude of the calculated solvent-induced shift becomes larger in the order of $SiCl_4$ (A_{calcd}=3.77)< $(CH_3)SiCl_3$ (A_{calcd}=4.73)<$(CH_3)_2SiCl_2$ (A_{calcd}=5.56)< $(CH_3)_3SiCl$ (A_{calcd}=7.03) as ε increases from 1.9 to 20.7. This means that as the number of substituted chlorine atoms is decreased, the value of parameter A_{calcd} is increased. The calculated results reproduce qualitatively the observed trend except for $(CH_3)_2SiCl_2$. Especially, for $SiCl_4$ the calculated chemical shift variation shows the smallest value compared with all the other compounds in going from ε=1.9 to 20.7. This result agrees qualitatively with the trend of the observed one. Therefore, it can be said that this is inactive in various solvent. The above results can be understood from the observed facts that the magnitude of dipole moment μ for these compounds[15] becomes in the order of $SiCl_4$ ($\mu\simeq$0)<$(CH_3)SiCl_3$ (μ=1.87)<$(CH_3)_2SiCl_2$ (μ=1.89)< $(CH_3)_3SiCl$ (μ=2.09) and therefore the magnitude of reaction field becomes in the same order. This means that the reaction field plays an important role in the solvent effect of ^{29}Si chemical shifts. Next, we discuss the solvent-induced ^{29}Si chemical shift variation of $(CH_3)_2HSiCl$, $(CH_3)HSiCl_2$, $HSiCl_3$, and $SiCl_4$ series. The magnitude of parameter A_{obsd} for them become larger in the order of $SiCl_4$<$HSiCl_3$<$(CH_3)HSiCl_2$ <$(CH_3)_2HSiCl$. The calculated results (A_{calcd}) reproduce this result. The calculated results[16] of their dipole moment show that the value of the dipole moment is increased in the order of $SiCl_4$ (μ=0)< $HSiCl_3$ (μ=1.0)<$(CH_3)HSiCl_2$ (μ=1.7)<$(CH_3)_2HSiCl$ (μ=1.8) as the number of substituted chlorine atoms is increased (the experimental data are unknown). Therefore, the above results can be explained reasonably by the same reason as the case of the first compound series.

Finally, we will consider the relationship between the ^{29}Si chemical shift and electron density as a function of the dielectric constant of the medium. In the previous work,[8] it is shown that the ^{29}Si chemical shifts move roughly downfield as an increase of the electron density on the silicon atom. The direction of such a shift is opposite to general consideration[14] that the increase of electron density leads to upfield shift. As seen from Table 2, the electron density on the silicon atom in the molecules considered here increase with an increase of ε. According to general consideration, this leads to upfield shift with an increase in ε. However, this is in disagreement with the observed results. Thus, it is apparent that such arguments must be done by the direct calculation of the ^{29}Si chemical shift as above mentioned.

From the above results, it can be concluded that the general trend found in this work would suggest the potential applicability of the FPT-CNDO/2 calculation with the "solvaton" model in interpreting solvent effects in aprotic polar media which influence ^{29}Si chemical shift.

References

1) I. Ando and G. A. Webb, *Org. Magn. Reson.*, **15**, 111 (1981).
2) G. Klopman, *Chem. Phys. Lett.*, **1**, 200 (1967).
3) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
4) H. A. Germer, Jr., *Theoret. Chim. Acta*, **34**, 145 (1974).
5) I. Ando, A. Nishioka, and M. Kondo, *J. Magn. Reson.*, **21**, 429 (1976).
6) I. Ando, Y. Kato, M. Kondo, and A. Nishioka, *Makromol. Chem.*, **178**, 803 (1977).
7) M. Jallali-Heravi and G. A. Webb, *Org. Magn. Reson.*, **13**, 114 (1980).
8) T. Takayama and I. Ando, *Bull. Chem. Soc. Jpn.*, **60**, 3125 (1987).
9) M. Kondo, I. Ando, R. Chujo, and A. Nishioka, *J. Magn. Reson.*, **24**, 315 (1976).
10) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca (1960), pp. 260.
12) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed by L. E. Sutton, Chemical Society, London (1958), Spec. Publ., No. 11.
13) J. A. Dean, "Lange's Handbook of Chemistry," McGraw-Hill, New York (1973), Section 10.
14) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford (1965), Vol. 1.
15) A. L. Mcclellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, San Francisco (1963).
16) For calculation from available bond moments, see: A. P. Altshuller and L. Rosenblum, *J. Am. Chem. Soc.*, **77**, 272 (1955).