Donor Number Estimation for Oxygen- and Nitrogen-Containing Solvents via Proton NMR Shift of Chloroform

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A linear correlation was determined for oxygen- and nitrogen-containing solvents between the proton NMR shift of chloroform, dilute in a solvent, and the donor number (DN) of that solvent. Results are given for water and for 13 organic solvents. The best straight line is given by $DN = 7.4 - 16.6 \, \Delta\delta \, (CHCl_3)$ where $\Delta\delta \, (CHCl_3)$ is the shift of pure chloroform relative to that of chloroform in dilute solution. Donor numbers of several solvents were estimated from the correlation.

1. INTRODUCTION

Many suggestions have been reported for characterizing solute-solvent interactions in liquid mixtures. One promising suggestion is provided by the donor-acceptor number concept described by Gutmann.[1] The donor number (DN) of a solvent is a measure of its electron donating ability. It can be used with the acceptor number to estimate infinte dilution activity coefficients, which in turn, can be used to estimate distribution coefficients and selectivities for solvent extrac-

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tion and other separation operations.[2] Donor numbers have been obtained by calorimetry using a $10^{-3}M$ solution of the donor solvent in 1,2-dichoroethane (with SbCl$_5$ as reference acceptor) for a limited number of compounds.[1]

Since calorimetry is not simple, requiring special equipment and extensive expertise, it is desirable to develop an alternate, experimental method for rapidly obtaining donor numbers of common organic solvents used in separation operations. Several solvent polarity scales which correlate with DN have been reviewed by Griffiths and Pugh.[3] However, none of the scales proposed there are useful for common organic solvents. Many of the scales use reference compounds with acceptor sites that are very different from those found in separation processes. For example, a ^{23}Na NMR shift correlation[4] predicts donor numbers for water and amines that are much higher than the measured values. A promising correlation based on the perturbation of the infrared O-D vibrational bands of methanol-d[5] is not applicable to solvents which contain a hydroxyl group.

Standard proton NMR with chloroform as the reference acceptor meets the objectives described above. Chloroform was selected because its acceptor strength is of the same magnitude as that of many industrial solvents, and because a previous study showed a large chemical shift difference between pure chloroform and chloroform in various ketones.[6] Chloroform is a poor donor and therefore self-association does not occur. The objective of this work is to establish a correlation between the chloroform proton NMR shift and the solvent donor number.
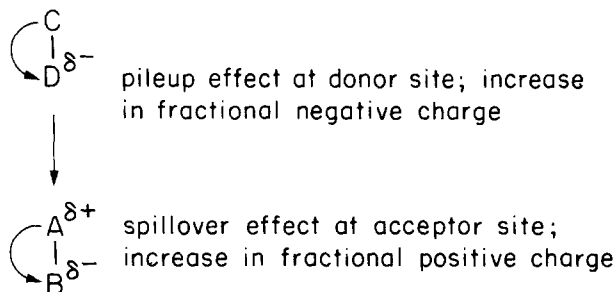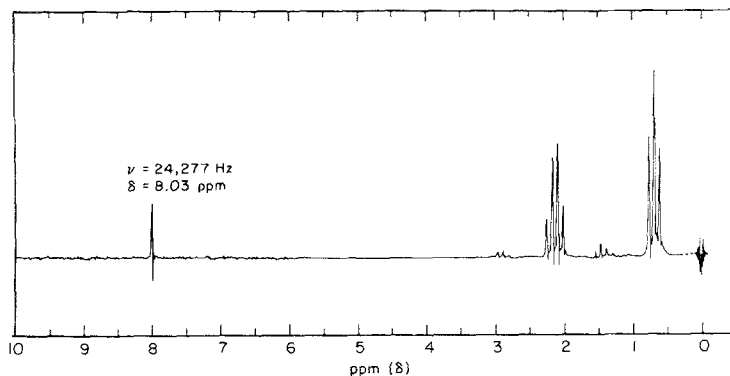

Fig. 1. Spillover Effect.

Fig. 2. NMR Spectra of 0.1*M* chloroform in triethylamine. Lock 0 ppm, spectrum amplification = 1000 for CHCl₃ and 30 for TEA, sweep from 10 to 0 ppm over 5 min.

2. THEORY

Molecular interaction between chloroform and the donor solvent decreases the electron shielding at the hydrogen of chloroform, according to the 'spillover effect' theory.[1] The original decrease of fractional positive charge at the acceptor atom is overcompensated by passing over the negative charge to other areas of the acceptor molecule in the spillover effect. The opposite, pileup effect occurs at the donor molecule as shown in Fig. 1. Thus, if the spillover effect theory is valid, the shift of chloroform in donor solvents should be downfield of the shift of pure chloroform since the acceptor hydrogen loses shielding. (The convention that the value of the shift increases with decreasing shielding is used throughout this article). The downfield shift should rise with increasing DN and should be more pronounced for a dilute solution wherein the isolated chloroform molecules are surrounded by solvent molecules.

3. EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental NMR sample-tube assembly consists of a 5 mm O.D. NMR tube, a reference capillary tube, and a teflon plug. The NMR tube contains the sample solution of 0.1*M* chloroform in the donor solvent. The capillary tube contains the reference solution of 25 wt% tetramethylsilane (TMS) in carbon tetrachloride.

Figure 2 shows an example of the spectra obtained from a Varian EM-390 90 MHz spectrometer with triethylamine as the donor solvent.

The observed chloroform peak corresponds to a shift of 8.03 ppm relative to TMS was obtained from

$$\delta\text{ (sample) } = [\frac{\nu\text{ (ref.) - }\nu\text{ (sample)}}{\nu\text{ (applied magnetic field)}}]10^6\text{ ppm}\qquad(1)$$

where δ is the shift and ν is the frequency. The triplet and quartet peaks near 1 and 2 ppm, respectively, are those of triethylamine.

The temperature at the probe was approximately 30°C. The solvents used in the experiment were of the highest purity available, which in most cases was spectrophotometric grade. Very small amounts of water and other impurities in the solvents may be responsible for some of the scatter in our data, but we are confident that they do not significantly affect the correlation. The observed shift is an average of the shifts for all of the chloroform protons present, as indicated by our results with solvent mixtures;[7] those results suggest that impurities (with different donor properties) must be present at levels of ~1% or more to have a significant effect on the observed shift. It has been pointed out to us that chloroform may contain HCl, which could affect the solvent properties and the chloroform shift. We have not investigated this effect; but we expect an averaging effect, as in our work with mixed solvents.

4. DATA REDUCTION

The NMR chemical shifts of chloroform in various solvents were measured at concentrations of 0.5, 0.3, and 0.1M chloroform. The chloroform shift for the 0.1M solution was assumed to be the infinite dilution value, since the concentration dependence of the shift in this range was negligible. (A small concentration dependence may appear for this concentration range with high-resolution NMR spectrometers, which operate at higher applied magnetic fields, but the added sensitivity is not significant here because it falls within the range of our experimental accuracy.) Since an external reference was used, the infinite dilution shift was corrected for bulk magnetic susceptibility. For a magnetic field perpendicularly directed to the axis of the cylindrical NMR tube

$$\delta\text{ (true) } = \delta\text{ (obs.) - }(2\pi/3)[\chi\text{ (ref.) - }\chi\text{ (sample)}]10^6\text{ppm}\qquad(2)$$

where χ is the volume magnetic susceptibility, a dimensionless quantity which is negative for diamagnetic substances. (If we had adopted the

Table I. Correlation Between Chloroform-Proton Shift
and Donor Number

Solvent	δ (obs)[a] (ppm)	$-\chi$[b]	$\Delta\delta$ (CHCl$_3$) (ppm)	Donor Number Meas.	Corr.
0 Chloroform	7.21	-	-	-	-
1 DCE [c]	7.61	0.744(5)	-0.29	0.(13)	12.2
2 Acetonitrile	7.33	0.527(5)	-0.47	14.1(13)	15.2
3 Dioxane	7.55	0.599(5)	-0.54	14.8(1)	16.4
4 PDC [d]	7.66	0.640(7)	-0.56	15.1(13)	16.7
5 Acetone	7.44	0.460(5)	-0.72	17.0(13)	19.4
6 Ethyl acetate	7.50	0.553(5)	-0.58	17.1(1,14)	17.0
7 Water	7.80	0.716(5)	-0.54	18.0(1,15)	16.4
8 THF [e]	7.72	0.624(8)	-0.65	20.0(15)	18.2
9 DMF [f]	8.03	0.502(7)	-1.22	26.6(13)	27.7
10 MPD [g]	8.43	0.644(7)	-1.28	27.3(1)	28.7
11 DMA [h]	8.30	0.603(5)	-1.28	27.8(15)	28.7
12 DMSO [i]	8.30	0.618(7)	-1.25	29.8(13)	28.2
13 Triethylamine	8.03	0.590(5)	-1.04	30.7(16)	24.7
14 HMPA[j]	9.13	0.675(7)	-1.96	38.8(15)	39.9

[a] Measured with 0.1M chloroform for all solvents except water, for which a saturated solution of chloroform in water was used. [b] Magnetic susceptibility per unit volume: $\chi =$ -0.692 for external reference solvent (CCl$_4$). [c] 1,2-Dichloroethane. Zero by definition of the DN scale: not included in the correlation for nitrogen and oxygen donors. [d] 1,2-Propanediol carbonate. [e] Tetrahydrofuran. [f] N,N-Dimethylformamide. [g] 1-Methyl-2-pyrrolidinone. [h] N,N-Dimethylacetamide. [i] Dimethylsulfoxide. [j] Hexamethyl-phosphoramide.

convention that the value of the shift increases with increasing shielding, the first minus sign in Eq. (2) would be a plus sign.) Magnetic susceptibilities are available for many substances.[8-10] Proton NMR methods can be used to measure unknown susceptibilities.[10,11] Estimates for susceptibilities can be calculated using Pascal's magnetochemical method.[12]

The difference between the pure chloroform shift and the true infinite dilution chloroform shift in a solvent [$\Delta\delta$ (CHCl$_3$) = δ (pure CHCl$_3$) - δ^∞ (CHCl$_3$,solvent)] was calculated for each solvent. The $\Delta\delta$ (CHCl$_3$) values were correlated with Gutmann's donor numbers for the solvents.[1,13-16]

The major sources of error in a particular $\Delta\delta$ (CHCl$_3$) value are the frequency reading corresponding to δ (obs.) and the bulk magnetic susceptibilities in Eq. (2). The frequency meter was accurate to within

Table II. Estimated Donor Numbers

Solvent	δ (obs) (ppm)	-χ	Δδ (CHCl$_3$) (ppm)	Donor Number
Cyclohexane	6.92	0.630(5)	0.16	4.8
n-Hexane	6.82	0.567(5)	0.13	5.3
n-Heptane	6.86	0.582(5)	0.12	5.4
1-Hexene	6.78	0.531(5)	0.09	5.9
CCl$_4$	7.34	0.692(5)	-0.13	9.6
1-Nitropropane	7.14	0.506(5)	-0.32	12.7
Formamide	7.40	0.580(5)	-0.43	14.6
Diethyl carbonate	7.52	0.622(5)	-0.46	15.1
Methanol	7.52	0.528(5)	-0.66	18.4
Cyclohexanone	7.77	0.632(6)	-0.69	18.9
Cyclohexanol	7.97	0.705(5)	-0.73	19.5
Ethylene glycol	8.01	0.695(5)	-0.80	20.7
THFA[a]	8.11	0.716(5)	-0.85	21.5
n-Butylamine	8.57	0.597(5)	-1.56	33.3

[a] Tetrahydrofurfuryl alcohol.

±1 Hz. To estimate the error in susceptibility, we considered high and low values as well as the author's 'best' values (marked with an asterisk) in Ref. 8. For susceptibilities from Ref. 10, the error range was estimated using the high and low values relative to the average value.

5. RESULTS

Table I shows experimental results for δ (obs.), χ, and Δδ (CHCl$_3$). The shifts are plotted against calorimetric donor number in Fig. 3. The best straight line is given by

$$DN = 7.4 - 16.6\Delta\delta \text{ (CHCl}_3) \tag{3}$$

with a correlation coefficient, $R^2 = 0.91$. Donor numbers calculated from the correlation are also listed in Table I.

Table II shows estimated donor numbers for some common solvents, calculated from the linear correlation. Calorimetric donor numbers have not been reported for these solvents.
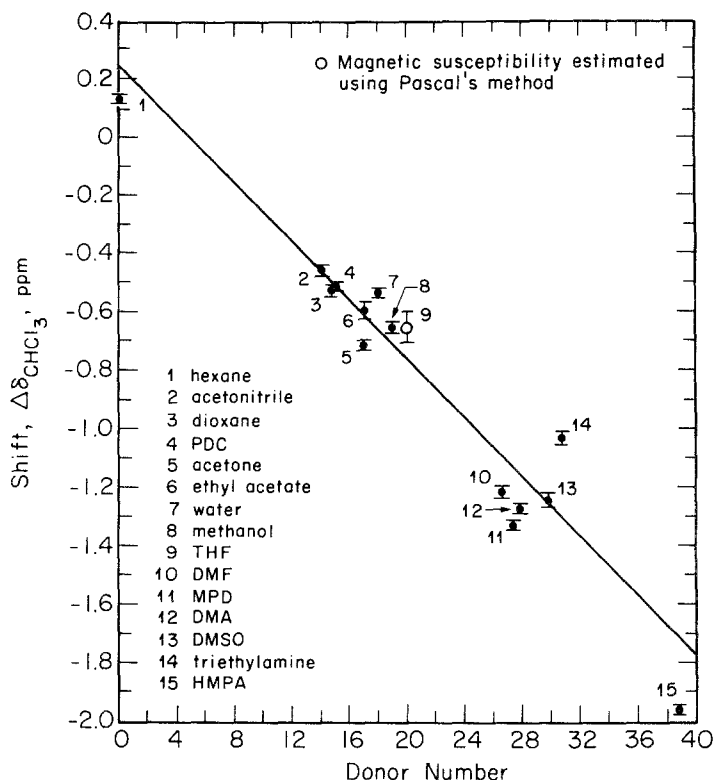
Fig. 3. Correlation of donor number with NMR shift of chloroform.

6. DISCUSSION AND CONCLUSION

The correlation between proton NMR shift of chloroform and donor number is reasonably successful for oxygen- and nitrogen-containing compounds with various functional groups. Unlike the ^{23}Na NMR shift correlation, the chloroform shift correlation gives reasonable agreement with calorimetric donor numbers for water and amines.

Reasonable donor number estimates are also obtained for hydrocarbons, but the estimated values for 1,2-dichloroethane and carbon tetrachloride are well above the expected values. The net shielding of the chloroform proton is the sum of five terms that may partially offset each other.[17] Our correlation of chemical shift with donor number assumes that one term, that due to specific interactions

between solvent and solute, dominates as the solvent is changed. For the case of solvents with large polarizable halogen atoms, such as carbon tetrachloride and 1,2-dichloroethane, the normally small contribution from van der Waals forces can become significant.[17] These forces would further decrease the shielding, which would give a larger shift and a larger predicted DN. All linear free energy relations are approximations which are only valid over a limited range. Our correlation should prove useful, however, for many industrial solvents with oxygen and/or nitrogen donor atoms; but extension to other solvents must be tested experimentally. For example, the proton NMR shift correlation for chloroform may not apply to aromatic compounds. Many aromatic solvents have proton NMR peaks near the field region of the chloroform peak so that the chloroform peak is difficult to distinguish. Moreover, a secondary magnetic field is generated by the circulation of π electrons around the periphery of the aromatic ring which weakens the local field above the ring. Thus, a chloroform molecule situated above the ring would shift downfield of one that was not.

ACKNOWLEDGMENT

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