

Measurement of Solvent Polarity by Nuclear Magnetic Resonance and Electron Spin Resonance Spectral Probes

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A detailed statistical analysis of data showing medium effects upon NMR shifts for ionic Lewis acids yielded no significant correlations in single and multiple parameter equations containing the dielectric constant and index of refraction of the solvent. By contrast, when the uncharged Lewis bases, fluoropyridines and alkyl nitroxide radicals, serve as the probes, an overall common order of increasing solvent polarity is apparent from correlations between ^{19}F NMR shifts and ^{14}N ESR hyperfine splitting constants. The greatest uncertainty within that order is among the hydrogen bonding solvents. Curvilinear and linear regression functions are obtained when the NMR and ESR parameters for the basic probes are correlated with empirical solvent polarity scales derived from red shift and blue shift solvatochromic indicators.

A number of empirical measures of solvent polarity have been derived from medium effects upon electronic transitions for model chromophores in the ultraviolet-visible region and on specific structural parameters for particular isotopic species as evaluated from NMR and ESR data. Although individual investigations have demonstrated some *overall* correlations between the Kosower Z or Dimroth-Reichardt E_T values and NMR chemical shifts (1) or ESR hyperfine splitting constants (2), the extent of scattering of data points along a given "best fit" regression line is often great, and comparisons among such solvent polarity parameters have been largely restricted to searches for pair-wise correlations within data sets. No correlations between NMR shifts and bathochromic indicator shifts have been attempted by other investigators.

From an analytical point of view, it would be desirable to enlarge the statistical interpretation of available data in order to differentiate clearly between general and specific effects of the solvent upon the probes and to obtain a better perspective on the limitations of such correlations. This report summarizes the tentative conclusions which can now be drawn from a more detailed statistical treatment of the extensive published data for a variety of probes in a wide range of solvent types.

The specific NMR and ESR data sources listed in Table I are classified in terms of the Lewis acid-base characteristics of the probes, and only those investigations involving ten or more solvents which included both polar aprotic and hydrogen bonding species were considered. It will be recognized that among the reference probes represented in Table I the range of acid-base strength is broad (from $^{23}\text{Na}^+$ as a weak electron pair acceptor to ^{19}F -pyridines as strongly basic donors). Data for proton shifts were excluded since others have already demonstrated that medium effects alone cannot be clearly resolved from proton NMR spectra (3).

Acid Probes. The observed changes in the NMR chemical shifts for the acidic probes (^{23}Na , ^7Li , ^{205}Tl salts) reflect the composite influences of the solvent upon ion pairing and on cation-solvent and anion-solvent interactions. However, for a restricted number of polar solvents in which ion pairing is negligible at low salt concentrations, the chemical shift for ^{23}Na is linearly related to the Gutmann donor numbers (4).

Similarly, ^7Li chemical shifts follow a linear function in the Kosower Z -values for five polar solvents (5). Even though the shift for ^{205}Tl is large and very sensitive to the solvent environment, no direct correspondence was found by Dechter and Zink (6) between the chemical shift and empirical solvatochromic or thermodynamic parameters.

Fowler, Katritzky, and Rutherford have deduced that changing dipolar and hydrogen bonding influences from the solvent can be more adequately described by multiple parameter functions involving dielectric constant (D), index of refraction (n), and solvent-induced spectral shifts (3). Equation 1 is representative of such a function in free energy ($f(\Delta G)$).

$$f(\Delta G) = \rho + \rho_H \left(\frac{n^2 - 1}{n^2 + 2} \right) + \rho_J \left(\frac{D - 1}{D + 2} \right) \quad (1)$$

The index of refraction term relates to the Dimroth-Reichardt values and the dielectric constant term to the hydrogen bonding interactions of both the solute probe and solvent. The ρ -values were designated as "sensitivity coefficients" (3).

The several forms of the equations which were summarized by Fowler, Katritzky, and Rutherford were applied to the NMR chemical shift data in the literature for MClO_4 ($\text{M} = \text{Li}^+, \text{Na}^+, \text{Tl}^+$), since the values for the chemical shifts of the perchlorates exhibit the least concentration dependence (4). When both polar aprotic and hydrogen bonding solvents are included, these multiple parameter correlation functions fail (regression coefficients less than 0.4) for all of the Lewis acid probes. Thus, although the magnitude and direction of the chemical shift for M(I) species frequently parallels anticipated changes in inner sphere solvation of the cation, the anion and concentration dependencies of the shifts permit only qualitative comparisons to empirical solvent polarity scales.

Base Probes. The ^{35}Cl NMR relaxation time for perchlorate ion in magnesium perchlorate ion pairs is quite sensitive to changes in the solvent, and the line width dependence upon concentration has been interpreted by Berman and Stengle in terms of solvent influences on ion pair dissociation processes (7). Only a qualitative correspondence was observed by Berman and Stengle between line widths and Gutmann donor numbers and/or the dielectric constants of the solvents, and important anomalies in solvent behavior were noted. When the data of these investigators were re-examined with the multiple parameter functions in dielectric constant and index of refraction summarized by Fowler, Katritzky, and Rutherford (3), no general or significant quantitative correlation to ^{35}Cl line widths was apparent.

The most fruitful data sources among the basic probes are the ^{19}F NMR shifts for the fluoropyridines in various solvents (1) and the solvent-influenced changes in the ^{14}N -hyperfine splitting constants (A_N) for the nitroxide group (2). For the former, solvent dependent changes in the magnitude and direction of the chemical shift are consistent with the relative orientation of the "reaction field" term for the solvent and the permanent dipole of the probe species (1). For 3-fluoropyridine in more polar solvents, deshielding arises from the alignment of the positive end of the solvent dipole toward the negative (or most basic) atom (i.e., F) in the probe molecule;

Table I. Summary of Major Experimental NMR and ESR Studies

Reference species	No. of solvents	Data tabulated	Literature source
Lewis acid probe			
²³ NaX as X = Br ⁻ , I ⁻ , SCN ⁻ , ClO ₄ ⁻ , BPh ₄ ⁻	10	²³ Na NMR chem. shift (NaCl aq. std)	Greenberg, Bodner, Popov (4)
⁷ LiX as X = Br ⁻ , ClO ₄ ⁻	11	⁷ Li NMR chem. shift (LiBr aq std)	Maciel et al. (5)
²⁰⁵ TlClO ₄	10	²⁰⁵ Tl NMR chem. shift (infinite dil aq std)	Dechter, Zink (6)
Lewis base probe			
³⁵ ClO ₄ ⁻ as: Li ⁺ , Na ⁺ , Mg ²⁺ salts	10	³⁵ Cl NMR relaxation time	Berman, Stengle (7)
2-, 3-, and 4-fluoropyridines; 4-fluoro-2-picoline	30	¹⁹ F NMR chem shift (C ₆ H ₅ F internal std)	Giam, Lyle (1)
Alkyl nitroxide free radicals: (1) di- <i>tert</i> -butyl nitroxide (2) 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (3) 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy	30	N-ESR hyperfine splitting const.	Knauer, Napier (2)

Table II. Spectroscopic Data Used in Correlations

Solvent	Electronic (<i>E_T</i>) ^a	N-ESR splitting const. (<i>A_N</i>) for:		¹⁹ F-NMR chem. shift for:	
		radical (1)	radical (2) ^b	2-F-py. ^c	3-F-py. ^c
1 Acetic acid	47.14	16.420	16.189	-43.24	10.72
2 Acetone	49.14	15.527	15.621	-45.43	13.65
3 Acetonitrile	48.97	15.666	15.761
4 Benzene	49.73	15.404	15.532	-46.12	13.71
5 Benzyl alcohol	...	16.266	16.286	-44.61	11.98
6 <i>n</i> -Butyl alcohol	47.19	16.018	16.038	-45.11	12.60
7 <i>tert</i> -Butyl alcohol	...	15.860	15.912	-45.31	12.77
8 Carbon disulfide	50.87	15.289	15.374	-45.73	13.96
9 Carbon tetrachloride	50.61	15.331	15.404	-46.39	13.96
10 Chlorobenzene	48.62	15.472	15.563	-45.80	13.53
11 Chloroform	48.13	15.863	15.775	-45.90	12.81
12 1,2-Dichloroethane	48.44	15.655	15.709
13 Diethyl ether	51.58	15.334	15.421	-46.09	14.09
14 <i>N,N</i> -Dimethylformamide	48.06	15.635	15.672	-45.25	13.55
15 Dimethyl sulfoxide	47.26	15.692	15.771	-44.81	13.40
16 1,4-Dioxane	50.07	15.452	15.539	-45.63	13.69
17 Ethyl alcohol	47.20	16.030	16.075	-45.02	12.40
18 Ethylene glycol	...	16.364	16.298	-44.34	11.94
19 <i>n</i> -Hexane	51.96	15.134	15.219	-46.29	14.32
20 Methyl alcohol	47.03	16.210	16.199	-44.79	12.08
21 Methylene chloride	48.46	15.752	15.775	-45.56	13.28
22 Nitromethane	48.39	15.759	15.858	-45.10	12.34
23 Isopentyl alcohol	...	16.004	15.961
24 Isopropyl alcohol	...	15.973	16.044	-45.17	12.61
25 Pyridine	47.98	15.608	15.663	-45.45	13.40
26 Tetrahydrofuran	48.72	15.373	15.474	-45.80	13.93
27 Toluene	...	15.347	15.461	-46.06	13.85

^a Combined results for Phenol blue (in kcal/mol) from J. Figueras, *J. Am. Chem. Soc.*, **93**, 3255 (1971); O. Kolling and J. Goodnight, *Anal. Chem.*, **45**, 160 (1973); O. Kolling, *Anal. Chem.*, **48**, 1221 (1976). ^b Hyperfine splitting constants for nitroxide radicals as designated by B. Knauer and J. Napier, *J. Am. Chem. Soc.*, **98**, 4395 (1976). ^c Values for ¹⁹F chemical shifts of fluoropyridines obtained by C. Giam and J. Lyle, *J. Am. Chem. Soc.*, **95**, 3235 (1973).

and, for 2-fluoropyridine as the probe, the positive end of the dipolar solvent is directed toward the nitrogen while the negative end shields the fluorine atom of the solute.

Because of these fundamental mechanistic differences in the responses of the fluoropyridine probes, the first new test applied to the ¹⁹F NMR data was to verify the compatibility of the chemical shift values from the two fluoropyridines with the same set of solvents. When their chemical shift values are plotted as in Figure 1, the greatest inconsistency in the correlation occurs among the hydrogen bonding solvents (1). If the most outlying points for dimethylformamide, chloroform, isopropyl- and *n*-butyl alcohols are excluded, a very respectable correlation coefficient of 0.984 is obtained. However, since

points for other hydrogen bonding solvents fall on the main linear sequence and are included in that coefficient, the numerical value of the correlation coefficient becomes less meaningful. Thus, the *exact* order for increasing polarity among the lower alcohols and chloroform becomes ambiguous when either of the fluoropyridines serves as the probe. A general failure of multiple parameter functions in dielectric constant and index of refraction to correlate with ¹⁹F chemical shifts in all of the solvents in Table II was demonstrated, as well, and parallels the conclusion of Giam and Lyle that the dielectric constant alone is an unsatisfactory measure of the influence of the solvent (1).

By contrast to the fluoropyridines, the effect of changes in

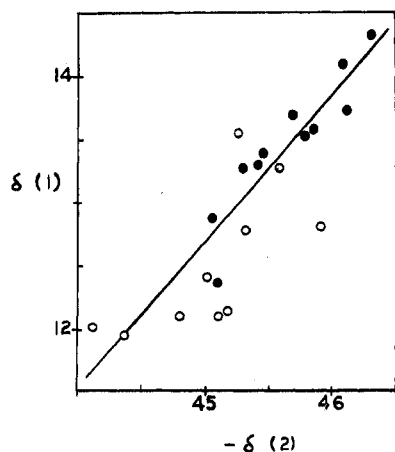


Figure 1. Scatter diagram for solvent-induced ^{19}F chemical shifts of 3-fluoropyridine (1) and 2-fluoropyridine (2). (O) Hydrogen bonding, (●) non-hydrogen bonding solvents

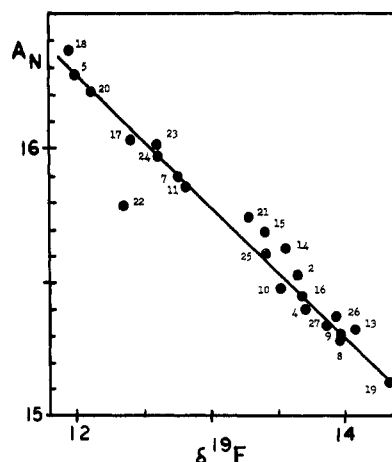


Figure 3. Comparison plot of A_N of di-*tert*-butyl nitroxide vs. ^{19}F chemical shift for 3-fluoropyridine for the solvents in Table II

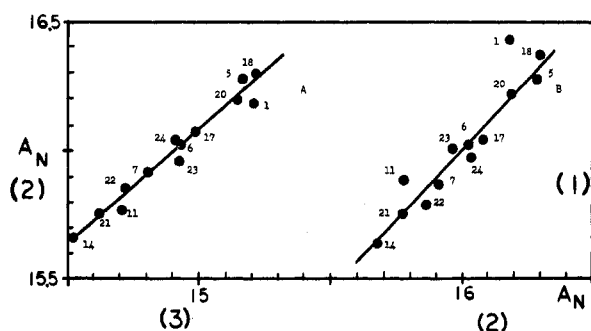
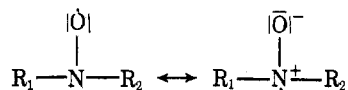


Figure 2. Scatter diagram for N -hyperfine splitting constants (A_N) for the nitroxide functional group in di-*tert*-butyl nitroxide (1), 4-amino-2,2,6,6-tetramethylpiperid-1-yloxy (2), and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (3) free radicals in hydrogen bond donor solvents

the solvent environment upon the ESR spectrum of the nitroxide group is fully consistent with a common mechanism for all of the free radical probes containing that functional group. The mechanistic conclusions of Knauer and Napier have been deduced from the electronic structural shift within the alkyl nitroxide species shown below (2).



A more polar medium enhances the negative charge density on the oxygen atom and simultaneously increases the spin density on the nitrogen. This effect is reflected in a corresponding increase in the magnitude of the nitrogen hyperfine splitting constant (A_N) with increasing polarity of the solvent. Although the A_N -values have been linearly correlated to the Kosower Z -function, the scattering of the data points is considerable and the correspondence is a semiquantitative one (2).

As was done with the NMR shifts for the fluoropyridines, the initial test applied to the ESR data in Table II was the pairwise comparison of the A_N values for the three nitroxide radical species in various solvents. The greatest scattering among the A_N data points occurs for the hydrogen bonding solvents; and the linear graphs for these (as shown in Figure 2) have correlation coefficients of 0.944–0.952, with less scattering from the lines than was found for the NMR data in Figure 1. The uncertainty in the experimentally derived A_N

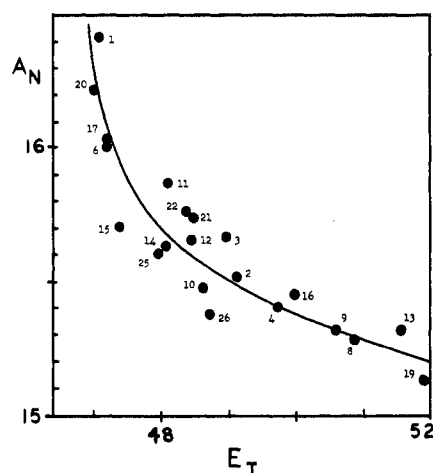


Figure 4. Correlation pattern for A_N of di-*tert*-butyl nitroxide with the transition energy (E_T in kcal/mol) for Phenol blue, using data for solvents in Table II

values was stated to be ± 0.01 – 0.03 unit (2); however, from the uncertainties in the linear slopes in Figure 2 and in the deviations of the correlation coefficients, the more realistic uncertainty appears to fall in the range ± 0.05 – 0.08 in hydrogen bonding media. The significance of this observation is illustrated by the clustering of the points for the lower alcohols. The comparisons among the three probes show that the order of polarity, $\text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > t\text{-C}_4\text{H}_9\text{OH}$, is quite definite; and, on the other hand, the real uncertainty in A_N does not allow the reliable placement of $i\text{-C}_3\text{H}_7\text{OH}$, $n\text{-C}_4\text{H}_9\text{OH}$, and $i\text{-C}_5\text{H}_{11}\text{OH}$ within that polarity order. Also, the reversal of the deviations of data points for chloroform and acetic acid (points 11 and 1) with respect to the lines in Figure 2 makes the sequential positions for these two important hydrogen bonding solvents very unclear.

Trial correlations were made between A_N values and ^{19}F NMR shifts of the fluoropyridines for all solvents common to the two data sets, and the linear plot in Figure 3 for A_N (di-*tert*-butyl nitroxide) vs. $\delta^{19}\text{F}$ (3-fluoropyridine) is representative of these functions. Correlation coefficients for such graphs ranged from 0.773 to 0.908 (Figure 3) with all solvents in Table II included except the consistently outlying points for acetic acid and nitromethane. Therefore, the comparisons of solvent polarity by the two types of probes appear to yield equivalent sequences for increasing polarity without discontinuities separating hydrogen bonding from nonpolar and/or

polar aprotic solvents. The most consistent correlations were found with 3-fluoropyridine as the NMR probe, and, as was noted above, the solvent effect on this molecule involves the least complex deshielding mechanism among the more basic probes.

Although the Kosower Z -values and the Dimroth-Reichardt transition energies have been used with some success in the original studies on NMR and ESR spectra, such functions often do not correlate well in single and multiple parameter comparisons for nonpolar and polar aprotic solvents. Krygowski and Fawcett (8) as well as others (3) have concluded that the Dimroth-Reichardt values are sensitive primarily to the Lewis acidity of the medium and to its hydrogen bond donor capacity. In view of the NMR vs. ESR spectral correlation in Figure 3, it is instructive to examine the data for possible relationships to transition energies of bathochromic indicators, since it has been demonstrated that such model chromophores are very responsive to changes in Lewis basicity of the solvent (9). Phenol blue was selected as a representative red shift indicator based upon previous theoretical and experimental investigations (9-11).

The curvilinear plot for the N-hyperfine splitting constant of di-*tert*-butyl nitroxide vs. the electronic $\pi \rightarrow \pi^*$ transition energy of Phenol blue is shown in Figure 4. Although the curve is nonlinear, the empirical trend places the stronger hydrogen bond donors in the upper left portion of the curve and nonpolar and weakly polar solvents toward the lower righthand extremity. The algebraic form of the correlation was established by empirical curve fitting techniques and was found to be the rational function given in Equation 2.

$$A_N = \frac{cE_T - a}{E_T - b} \quad (2)$$

When using the specific data in Table II relating A_N (di-*tert*-butyl nitroxide) and E_T (Phenol blue), the constants have the values: $a = 712.7 \pm 0.11$; $b = 46.7 \pm 0.03$; $c = 15.27 \pm 0.32$ (std dev). The computation of these constants was initiated with assumed graphic values for b as one of the asymptotes and was followed by iteration until convergence in

c and a was achieved. As a predictive function, Equation 2 carries an uncertainty of ± 0.09 (std dev) in the derived values of A_N . Based upon 20 solvents (excluding only the statistically rejected point for diethyl ether), the correlation coefficient is 0.885 for the nonlinear regression. Superficially, the same form of correlation function is obtained when A_N values for the other nitroxide radical probes are used; however, the extent of scattering of the data points is greater than in Figure 4 so that additional ESR probe-dependent constants in the equation cannot be reliably evaluated.

To summarize, it is evident that the NMR and ESR spectral responses to medium effects given by the specific Lewis bases, 3-fluoropyridine and di-*tert*-butyl nitroxide radical, yield the best overall correlations to other solvent polarity parameters. Although single and multiple parameter correlations involving macroscopic solvent properties generally fail, pairwise comparisons of NMR or ESR data to electronic spectral shifts for solvatochromic indicators give rise to approximately the same order for increasing solvent polarity. Recent values for ^{31}P NMR coupling constants ($^1J_{\text{Pt-P}}$) of *trans*-[PtCl₂(PBU₃)₂] in ten aprotic solvents (12) correlate linearly to the ESR splitting constants for the nitroxide group and to the ^{19}F chemical shifts as well. However, the greatest uncertainties in the polarity sequence remain among the hydrogen bond donor solvents, regardless of the NMR probe used.

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Determination of Hydrogen Content of Fuel by Low Resolution Proton Nuclear Magnetic Resonance Spectrometry

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A preliminary evaluation is reported of the use of low resolution nuclear magnetic spectrometry (NMR) for determination of the hydrogen content of aviation turbine fuels. With correct choice of instrument conditions, the technique is shown to be accurate and simple to use, and to require a comparatively short time for determination.

Combustion characteristics of aviation turbine fuels are controlled by a large number of tests in fuel specifications. American Society for Testing and Materials (ASTM) and

International Air Transport Association (IATA) specifications (1, 2) include tests for aromatic content, naphthalene content, smoke point, and luminometer number. Increasingly, however, fuel hydrogen content has been shown by many workers to give better predictions of combustion performance and it has been proposed (e.g. 3) that a single determination of hydrogen content could be used to replace the present multiplicity of tests. Both ASTM and IATA are considering this proposal at present and therefore it was considered opportune to examine methods for its determination.

To date these methods have been based on complete combustion of a fuel sample with gravimetric determination of the