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UV/Vis Spectroscopic Evaluation of 4-Nitropyridine *N*-Oxide as a Solvatochromic Indicator for the Hydrogen-Bond Donor Ability of Solvents

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The potential of 4-nitropyridine *N*-oxide to act as a solvatochromic indicator of the hydrogen-bond donor ability of solvents has been evaluated. A linear free-energy relationship has been established that is predominantly dependent on the Kamlet−Taft α parameter of the solvent. In comparison to the previously reported results obtained for pyridine *N*-oxide, 4-nitropyridine *N*-oxide possesses a solvatochromic effect that is located in the long wavelength ultraviolet region ($\lambda = 330-355$ nm) of the spectrum, making it a viable probe for hydrogen-bond donation assessment.

Introduction

UV/vis spectroscopic measurement of charge-transfer maxima of probe solutes in solution is known to provide numerical values for the intermolecular interactions between solute and solvent. The most extensively applied method of generating values for intermolecular solute/solvent interactions is the method of Kamlet and Taft.[1−3] The Kamlet−Taft parameters are α, the hydrogen bond donation ability of the solvent, β, the hydrogen-bond acceptance ability of the solvent, and π^*, a parameter that describes the dipolarity and polarizability of the solvent. Using linear free-energy relationships (LFER), the Kamlet−Taft parameters can effectively model processes in solution according to the general expression

$$\mathrm{XYZ} = \mathrm{XYZ}^\circ + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

where XYZ is the value of the solvent-dependent process to be modeled, XYZ°, s, d, a, and b are the coefficients determined from the LFER analysis, and δ is a polarizability adjustment term. The δ term is dependent on the class of solvent to be studied; for aromatic solvents $\delta = 1$, for polyhalogenated solvents $\delta = 0.5$, and for all other solvents $\delta = 0$. Such LFER approaches have found success in modeling solution processes as diverse as solubility,[4] partition coefficients,[5] and chromatographic retention.[6] Analysis of the coefficients of the LFER provide insight into the dominant solute/solvent interactions involved in a particular solvent-dependent process.

As suggested by Kamlet and Taft, the determination of the β and π^* parameters using solvatochromic peak maxima of select probe solutes is relatively straightforward. A value of π^* for a particular solvent can be directly calculated from the $\pi \rightarrow \pi^*$ transition maximum of a dissolved small organic probe, such as 4-nitroanisole. Similarly, by measuring the $\pi \rightarrow \pi^*$ transition maximum of a second small dissolved organic probe, such as 4-nitrophenol, in conjunction with the peak maximum for 4-nitroanisole, a value of β for the solvent of interest can be calculated. The relationship can be understood in terms of a LFER, in that the transition maximum of 4-nitroanisole will not include contributions from the α and β terms of eq 1. Replacement of the methoxyl group of 4-nitroanisole by the hydroxyl group of 4-nitrophenol results in a probe solute that is capable of hydrogen-bond donation and the β term of the LFER assumes a nonzero value.

In contrast to the β and π^* parameters, α is traditionally determined using large organic or organometallic probes,[3] due to the extensive use of these probes as polarity indicators of solvents. Often these large probes are insoluble in fluorinated solvents.[7,8] In our laboratory, we are in the process of determining the Kamlet−Taft parameters for alternative solvents which may be useful as replacements for chlorinated solvents. Many of the alternative solvents possess a high degree of fluorination (but no chlorine or bromine) resulting in zero ozone depletion potential by currently acceptable mechanisms. As a potential solution to the solubility problem encountered when using conventional UV/vis spectroscopic acidity probes in fluorinated solvents, the replacement of the methoxyl group of 4-nitroanisole with a group that is capable of hydrogen-bond acceptance is desirable. Such an approach was undertaken using pyridine *N*-oxide;[9] however, the $\pi \rightarrow \pi^*$ transition maxima observed ($\lambda = 283-254$ nm) resided in the absorption region of many solvents themselves, thus detracting from the spectroscopic utility of the probe. Recognizing the potential utility of pyridine *N*-oxide as an acidity probe, the ^{13}C NMR chemical shift of pyridine *N*-oxide was used to establish a LFER that was related solely to a dependence on α.[10]

A probe that would more closely resemble the nitroaromatics typically used in the Kamlet and Taft approach,

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Table 1. Maximum of the $\pi \rightarrow \pi^*$ Transition of 4-Nitropyridine *N*-Oxide in the 48 Solvents Studied and the π^*, a, b and d parameters of the solvent taken from reference 16

no.	solvent	ν_{max} (kK) ± 2σ	π^*	α	β	δ
1	*n*-heptane	28.80 ± 0.02	−0.08	0	0	0
2	*n*-hexane	28.92 ± 0.04	−0.04	0	0	0
3	*n*-pentane	28.89 ± 0.04	−0.08	0	0	0
4	cyclohexane	28.71 ± 0.02	0	0	0	0
5	triethylamine	28.66 ± 0.02	0.14	0	0.71	0
6	diethyl ether	28.72 ± 0.02	0.27	0	0.47	0
7	tetrachloroethene	28.59 ± 0.02	0.28	0	0.05	0.5
8	carbon tetrachloride	28.79 ± 0.02	0.28	0	0.10	0.5
9	1-chlorobutane	28.87 ± 0.04	0.39	0	0	0
10	*p*-xylene	28.31 ± 0.02	0.43	0	0.12	1
11	mesitylene	28.26 ± 0.02	0.41	0	0.13	1
12	*m*-xylene	28.33 ± 0.02	0.47	0	0.12	1
13	1,1,1-trichloroethane	28.77 ± 0.02	0.49	0	0	0.5
14	trichloroethene	28.79 ± 0.02	0.53	0	0.05	0.5
15	toluene	28.38 ± 0.04	0.54	0	0.12	1
16	1,4-dioxane	28.59 ± 0.02	0.55	0	0.37	1
17	ethyl acetate	28.74 ± 0.02	0.55	0	0.45	0
18	*p*-difluorobenzene	28.85 ± 0.02	0.58	0	0.03	1
19	tetrahydrofuran	28.52 ± 0.02	0.58	0	0.55	0
20	benzene	28.43 ± 0.02	0.59	0	0.11	1
21	methyl acetate	28.80 ± 0.02	0.60	0	0.42	0
22	fluorobenzene	28.67 ± 0.02	0.62	0	0.07	1
23	cyclohexanone	28.44 ± 0.02	0.76	0	0.53	0
24	1,2-dichloroethane	28.71 ± 0.02	0.81	0	0.10	0.5
25	pyridine	28.30 ± 0.02	0.87	0	0.64	1
26	*N*,*N*-dimethylformamide	28.46 ± 0.02	0.88	0	0.69	0
27	dimethyl sulfoxide	28.43 ± 0.03	1.00	0	0.76	0
28	*sec*-butyl alcohol	30.11 ± 0.02	0.40	0.69	0.80	0
29	octanol	30.02 ± 0.02	0.40	0.77	0.81	0
30	isobutyl alcohol	30.31 ± 0.02	0.40	0.79	0.84	0
31	hexanol	30.03 ± 0.02	0.40	0.80	0.84	0
32	pentanol	29.98 ± 0.02	0.40	0.84	0.86	0
33	isopentyl alcohol	30.12 ± 0.02	0.40	0.84	0.86	0
34	*tert*-butyl alcohol[a]	30.17 ± 0.02	0.41	0.62	0.93	0
35	decanol	30.00 ± 0.02	0.45	0.70	0.82	0
36	*n*-butyl alcohol[a]	30.08 ± 0.04	0.46	0.79	0.84	0
37	isopropyl alcohol[a]	30.18 ± 0.02	0.51	0.80	0.84	0
38	ethanol	30.23 ± 0.04	0.54	0.86	0.75	0
39	chloroform	29.20 ± 0.04	0.58	0.20	0.10	0.5
40	methanol	30.46 ± 0.02	0.60	0.98	0.66	0
41	2-butanone	28.71 ± 0.04	0.67	0.06	0.48	0
42	acetone	28.79 ± 0.02	0.71	0.08	0.43	0
43	aniline	28.81 ± 0.04	0.73	0.26	0.50	1
44	acetonitrile[a]	28.98 ± 0.02	0.85	0.15	0.40	0
45	dichloromethane	28.88 ± 0.02	0.82	0.13	0.10	0.5
46	benzyl alcohol	29.84 ± 0.02	0.98	0.60	0.52	1
47	acetic acid	31.85 ± 0.02	0.64	1.12	0.45	0
48	water	31.76 ± 0.02	1.09	1.17	0.47	0

[a] Indicates that the values for α and π^* were taken from reference 9.

yet still retain the desirable functionality of the pyridine *N*-oxide probe, is 4-nitropyridine *N*-oxide. Addition of a nitro group to the previously investigated pyridine *N*-oxide would produce a bathochromic shift of the peak maximum due to increased ring conjugation, resulting in a greater spectroscopic utility for the probe. It is the purpose of this study to measure the peak maxima of 4-nitropyridine *N*-oxide in various solvents and optimize the LFER using Kamlet−Taft parameters as the dependent variables.

Experimental Section

Chemicals. 4-nitropyridine *N*-oxide (purity 97%) was obtained from a commercial supplier and was vacuum desiccated over $CaSO_4$ prior to use due to the hygroscopic nature of the compound. Solvents were obtained from commercial suppliers and were of spectroscopic purity or better and were used as received.

Measurement of Solution Spectra. A commercially available dual-beam high-resolution UV/vis spectrophotometer was used to determine the peak maximum of the transition for 4-nitropyridine *N*-oxide in the solvents. The neat solvent was placed in a 1 cm quartz reference cuvette, and a small amount of 4-nitropyridine *N*-oxide was placed in the matched sample cuvette and filled with solvent. The solution in the sample cuvette was shaken until a constant absorbance value was obtained. The 4-nitropyridine *N*-oxide solution was then either diluted with the solvent or several more crystals were added to the solution to adjust the absorbance value to between 0.2 and 1.8 absorbance units. The spectrum of 4-nitropyridine *N*-oxide in the solvent was scanned at a resolution of 0.05 nm per data point. The peak maximum was determined both by a peak detection algorithm of the spectrophotometer software package and by visual confirmation by the operator using an unsmoothed spectrum. Five spectra were measured for 4-nitropyridine *N*-oxide in each solvent and the average value of the transition maxima computed.

Results and Discussion

Results of the $\pi \rightarrow \pi^*$ transition of 4-nitropyridine *N*-oxide in the solvents studied are given in Table 1. The ν_{max} value is expressed in kilokaysers ($1\ \mathrm{kK} = 10^{-4}\ \mathrm{nm}^{-1}$) along with the standard uncertainty, σ, multiplied by a coverage factor,[11] $k = 2$. The probe was soluble in all classes of solvents studied. Within the framework of eq 1, multiple LFER equations were computed to examine the data collected. It was concluded that the experimental ν_{max} value in solvents **47** and **48** would not be included in any further regression equations because the values deviated significantly (greater than three standard deviations) from the best LFER using all the data. A possible explanation for the poorer correlation of the transition maxima in solvents **47** and **48** is that 4-nitropyridine *N*-oxide may not be sufficiently basic to offset the self-association of these solvents,[12] or 4-nitropyridine *N*-oxide may be simply protonated in solvent **47**.

The following LFER set was computed for the remaining 46 solvents using different combinations of the Kamlet−Taft parameters as independent variables.

$$\nu_{max}\,(\mathrm{kK}) = 28.8334 - 0.0388\,(\pi^* + 6.3634\delta) + 2.0062\alpha - 0.3429\beta \quad (n = 46,\ r = 0.978,\ \mathrm{SD} = 0.1497) \qquad (2)$$

$$\nu_{max}\,(\mathrm{kK}) = 28.7885 - 0.1951\,(\pi^* + 0.8006\delta) + 1.8371\alpha \quad (n = 46,\ r = 0.973,\ \mathrm{SD} = 0.1652) \qquad (3)$$

$$\nu_{max}\,(\mathrm{kK}) = 28.7595 - 0.2681\pi^* + 1.9062\alpha \quad (n = 46,\ r = 0.969,\ \mathrm{SD} = 0.1743) \qquad (4)$$

Examination of the standard error and *t*-value of the β term showed that it was not a statistically significant variable in the regression equation. This is to be expected from a probe, such as 4-nitropyridine *N*-oxide, that is incapable of hydrogen-bond donor abilities. The

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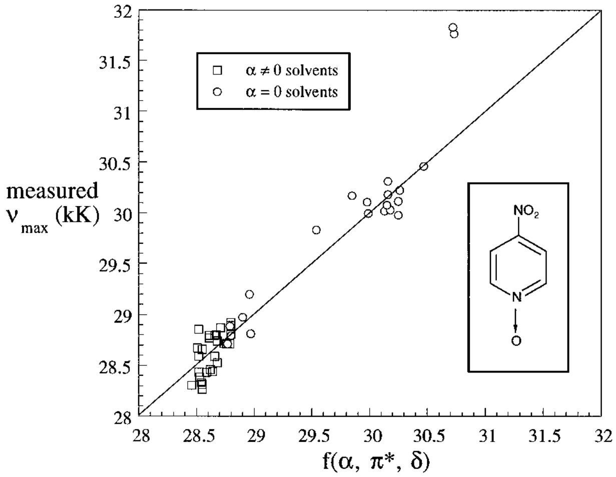

Figure 1. Linear correlation of the experimental UV/vis absorption maxima and the predicted values according to eq 3. Points for solvents **47** and **48** are included in the plot, but not in the regression equation. The inset shows the chemical structure of 4-nitropyridine *N*-oxide.

positive charge at the pyridinium nitrogen is resonance delocalized about the ring for poorer electron acceptor ability of the probe. A LFER using solely α and π^* as the independent variables, as in eq 4, results in separate LFERs among the solvent classes measured. Therefore, inclusion of the δ term in eq 3 was deemed necessary to account for the variation in polarizability among the various solvent classes. The correlation is graphically depicted using eq 3 in Figure 1.

The *a*/*s* coefficient ratio in eq 3 is 9.42 indicating that the hydrogen-bond donor ability of the solvent is the predominant solute/solvent interaction on the solvatochromic activity of 4-nitropyridine *N*-oxide. This is manifest in the relative insensitivity of the position of the peak maximum of the $\pi \rightarrow \pi^*$ transition[13] to the solvents incapable of hydrogen-bond donation. In fact, a good correlation exists for the solvents capable of hydrogen-bond donation using only the α term as an independent variable.

$$\nu_{\max}\,(\mathrm{kK}) = 28.6578 + 1.8615\alpha$$
$$(n = 19,\ r = 0.967,\ \mathrm{SD} = 0.1593) \qquad (5)$$

According to the Franck–Condon principle, although the dipole moments of the excited state, μ_e, and ground state, μ_g, are different, the positions of the nuclei of the excited state solute and the nuclei of the surrounding solvent molecules should not change on the time scale of the electronic transition. The dipole moment of 4-nitropyridine *N*-oxide in the ground state was calculated to be 0.09 D.[14] The hypsochromic band shift observed in solvents capable of hydrogen-bonding can be attributed to the increased stabilization of the electronic ground state relative to the excited state of 4-nitropyridine *N*-oxide ($\mu_g > \mu_e$).[15]

Considering all LFER equations, we recommend that eq 3 be used in computing α values using 4-nitropyridine *N*-oxide as a probe. Both the π^* and α terms contribute to the measured transition maxima in solution; however, the dominant term is clearly the α term. Although the transition maxima appears to also depend on solvent class, addition of the δ term appears to correct for the polarizability of the solvent classes and is not an additional experimentally determined quantity. In comparison to the aforementioned results obtained for pyridine *N*-oxide, 4-nitropyridine *N*-oxide possesses a solvatochromic effect that is located in the long wavelength ultraviolet region (λ = 330–355 nm) of the spectrum, making it a viable probe for hydrogen-bond donation assessment.

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