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Linear Solvation Energy Relationships. 18. Solvent Effects on the Electronic Absorption Spectrum of *p*-Nitrophenoxide Ion

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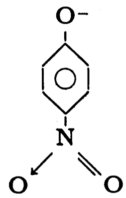
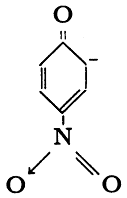
A quantitative analysis of the effects of hydroxylic and aprotic solvents on the electronic absorption spectrum of 4-nitrophenoxide anion is described. By means of linear solvation energy relationships, the contributions of solvent dipolarity, polarizability, and hydrogen bonding are assessed. A significant conclusion is that ion-pairing strongly influences the 4-nitrophenoxide ion in aprotic solvents, but not in hydroxylic solvents. In the latter, specific solvation of both the nitro group and the phenoxide ion center are important.

The last two decades have witnessed a steady effort in the field of study of solvent effects on the UV-visible spectra of polar solutes. An important result of this work has been the development of a number of empirical solvent polarity scales.¹⁾ Recently, the ability of bulk solvents to act as proton donors in hydrogen bonding interactions has also been quantified.²⁾ Although a number of questions still remain unanswered, we feel that sufficient information is already available to allow the use of these scales in order to gain structural and mechanistic information. Thus the π^* scale of solvent dipolarity/polarizabilities³⁾ and the α scale of solvent HBD (hydrogen bond donor) acidities²⁾ have been extensively used⁴⁾ to analyze solvent effects on physical properties and chemical reactivity.

Ueji and Kitadani (henceforth abbreviated as U. and K.) have recently described in this journal the influence of solvents on the absorption spectrum of sodium *p*-nitrophenoxide.⁵⁾ By adding substantial amounts of 15-crown-5, these authors were able to obtain the spectrum in a wide variety of solvents. The frequencies, $\nu(\mathbf{1})_{\max}$, corresponding to the $\pi\rightarrow\pi^*$ electronic transition of 4-nitrophenoxide ion (represented by canonical structures **1a**—**d**) in a number of solvents are given in Table 1, together with solvent π^* and α values.


1a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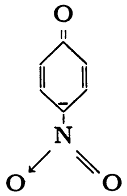
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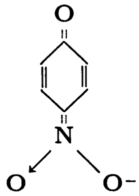

1d

Inspection of the $\nu(\mathbf{1})_{\max}$ values shows two different effects: one is a bathochromic shift with increasing solvent dipolarity/polarizability; the other is a hypsochromic shift with increasing HBD acidity of the solvent. U. and K. have pointed out and discussed both effects. While we basically agree with their interpretation of the experimental results, we wish to reexamine them from a somewhat more quantitative standpoint. Our aim is to demonstrate that, when solvent dipolarity, polarizability, and hydrogen bonding effects on $\nu(\mathbf{1})_{\max}$ are unravelled by means of the solvatochromic comparison method, the same experimental data can be made to yield additional important information regarding the detailed nature of the electronic transition.

Results and Discussion

When hydrogen bonding effects are excluded, as when solute and solvent are both non-hydrogen bond donors, solvent effects on electronic spectra can take either of two forms. For $p\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of uncharged indicators with all solvents considered together, and for other types of electronic transitions when families of solvents with similar polarizability characteristics are treated separately (*e.g.*, only non-chlorinated aliphatic solvents, only polychlorinated aliphatics, or only aromatic solvents) the linear solvation energy relationship (LSER) takes the form,

$$\nu(i)_{\max} = \nu(i)_0 + s\pi^*, \tag{1}$$

where s is a measure of the response of $\nu(i)_{\max}$ to solvent dipolarity. For the other electronic transitions, when all solvents need to be considered together, the appropriate form of the LSER is,

$$\nu(i)_{\max} = \nu(i)_0 + s(\pi^* + d\delta), \tag{2}$$

where δ, a 'polarizability correction term' $=0.0$ for non-chlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.

Solvent Dipolarity/Polarizability Effects. Considering first the $\nu(\mathbf{1})_{\max}$ values in the six non-protic aliphatic solvents of Table 1 according to Eq. 1, the regression equation with π^* is,

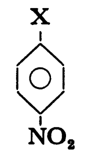
$$\nu(\mathbf{1})_0 = (26.71 - 3.99\pi^*) \times 10^3\ \mathrm{cm}^{-1}, \tag{3}$$

$$r\ \text{(the correlation coefficient)} = 0.980,$$

$$sd\ \text{(the standard deviation)} = 0.24 \times 10^3\ \mathrm{cm}^{-1}.$$

The ν_0 and s values in Eq. 3 provide important mechanistic information. Thus, it is evident from the shift to lower absorption frequencies with increasing π^* that the electronic transition is from a ground state which is relatively more charge-diffuse to an electronic excited state which is relatively more charge-concentrated.

It is profitable to consider Eq. 3 in the context of solvent effects equations for corresponding spectral bands of related indicators as, for example, the $[{}^+\mathrm{X}{=}\mathrm{C}(4)\rightarrow\mathrm{C}(1){=}\mathrm{NO_2}^-]$ electronic transitions of the 4-substituted nitrobenzenes, **2**—**7**, which we reported



2, $X=Me_2N-$ **5**, $X=C_2H_5-$
3, $X=H_2N-$ **6**, $X=F-$
4, $X=MeO-$ **7**, $X=H-$

earlier.[1d] It was then shown that the $\nu(i)_0$ and s values in the solvatochromic equations for **2**—**7** are linear with the substituent σ^+ values, the correlation equations being,

$$\nu(i)_0 = (6.39\sigma^+ + 39.50) \times 10^3\,\text{cm}^{-1}, \tag{4}$$

and

$$s = 1.021\sigma^+ - 1.685. \tag{5}$$

In order to ascertain whether 4-nitrophenoxide conforms with these relationships, we have back-calculated values of σ^+ for the 4-oxy substituent by substituting the $\nu(\mathbf{1})_0$ and s terms from Eq. 3 into Eqs. 4 and 5, and compared the results with independent estimates of the value of this substituent constant. The $\nu(\mathbf{1})_0$ value of 26.71 in Eq. 4 calls for a σ^+ of -2.00, while the s value of -3.99 in Eq. 5 is consistent with $\sigma^+=-2.25$. For comparison, Hine[6] has reported that σ^+ for the *p*-O^- substituent is -2.3, with the comment that σ^+ values for electrically charged substituents are relatively less reliable, being dependent to some extent on solvation and ion pairing.

The at least approximate conformance of 4-nitrophenoxide with Eqs. 4 and 5 indicates that, as with **2**—**7**, the direction of charge migration in the electronic excitation is away from the *p*-substituent and towards the nitro group. Taken with the finding that there is concentration of charge in the electronic excitation, this leads to the conclusion that electron density in the ground state is delocalized into canonical structures like **1a**—**d** (with **1a** probably being the dominant contributor), whereas in the electronic excited state charge is redistributed and concentrated into canonical structures like **1c** and **1d** (with **1d** being the dominant contributor).

If the data in the non-protic aliphatic, polychloroaliphatic, and aromatic solvents of Table 1 are considered together, the appropriate form of the linear solvation energy relationship is given by Eq. 2. The d value is calculated to be -0.26,[7] and the least squares correlation of $\nu(\mathbf{1})_{\max}$ with $(\pi^*-0.26\delta)$ leads to the regression equation,

$$\nu(\mathbf{1})_{\max} = \{26.67 - 3.93(\pi^*-0.26\delta)\} \times 10^3\,\text{cm}^{-1}, \tag{6}$$
$$n = 11,\ r = 0.988,\ sd = 0.17 \times 10^3\,\text{cm}^{-1}.$$

A plot of $\nu(\mathbf{1})_{\max}$ against (π^*-0.26δ) is shown in Fig. 1.

Since we have shown earlier[1d,7] that the d value in Eq. 2 is effectively zero for the $\pi\rightarrow\pi^*$ transitions of indicators **2**—**7**, it is necessary to inquire why d should have a large negative value for the corresponding transition of indicator **1**. This is particularly important because, in all correlations of electronic spectra which we have hitherto carried out, the general conclusion had been that solvatochromic equations reflected either of two patterns of behavior: (a) If $\nu_{\max}$ was shifted bathochromically with increasing solvent dipolarity/polarizability, as was usually the case

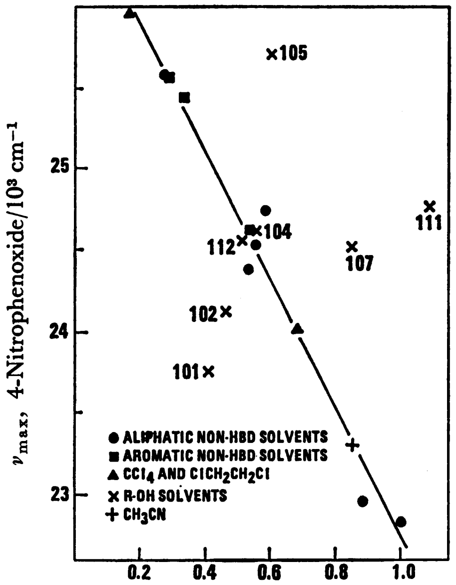


Fig. 1. $\nu(\mathbf{1})_{\max}$ plotted against $(\pi^*-0.26\delta)$.

for $\pi\rightarrow\pi^*$ transitions of uncharged indicators, d in Eq. 2 was zero. (b) For all spectra shifted hypsochromically with increasing solvent π^* values, as was usually the case for $n\rightarrow\pi^*$ transitions of uncharged indicators and $\pi\rightarrow\pi^*$ transitions of zwitterionic indicators, d was always finite and negative. 4-Nitrophenoxide is the first example we have investigated of an anionic indicator, and it is of interest that it follows still a third pattern of behavior, *i.e.*, a bathochromic shift with increasing solvent π^* values coupled with a large negative value of d in Eq. 2.

We had earlier suggested[1d,7] that d is zero when the indicator dipole does not change direction in the electronic excitation (so that solvent molecules which are optimally situated to solvate the indicator ground state are also well oriented to solvate the excited state). Finite negative values of d had been associated with transitions wherein the direction of the indicator dipole changed in the electronic transition and, in conformance with the Franck-Condon principle, solvent molecules which were well situated to solvate the ground state were poorly oriented to solvate the excited state. On this basis the large negative d value for **1** suggests that the dipole changes direction in the electronic excitation and is consistant with canonical structure **1a** being the dominant contributor to the ground state and **1d** the dominant excited state contributor.

Effects of Hydrogen Bonding by Protic Solvents. The correlations become particularly interesting when we consider the HBD (hydrogen bond donor) solvents, $\nu(\mathbf{1})_{\max}$ values for which are also plotted in Fig. 1, where it is evident that they do not conform with the correlation with $(\pi^*-0.26\delta)$. We denote the vertical displacements of the HBD solvent data points from the regression line by $\Delta\Delta\nu(\mathbf{1}-\pi^*)$, and we define this quantity as the additional shift in $\nu(\mathbf{1})_{\max}$ caused by hydrogen bonding to **1** by the solvent after the solvent dipolarity/polarizability effects have been accounted for by a correlation with the π^* scale. We

Table 1. Solvent effects on the spectrum of 4-Nitrophenoxide anion (**1**)

No.[a]	Solvent	π^*	α	$\nu(\mathbf{1})_{\max}/10^3\ \mathrm{cm}^{-1}$	$\Delta\Delta\nu(\mathbf{1}-\pi^*)/10^3\ \mathrm{cm}^{-1}$
7	Diethyl ether	0.27	0.00	25.58	
9	Dioxane	0.55	0.00	24.54	
13	Tetrahydrofuran	0.58	0.00	24.75	
61	1,2-Dimethoxyethane	0.53	0.00	24.39	
23	*N*,*N*-Dimethylformamide	0.88	0.00	22.96	
29	Dimethyl sulfoxide	1.00	0.00	22.83	
6	Carbon tetrachloride	0.29	0.00	25.97	
20	1,2-Dichloroethane	0.81	0.00	24.03	
8	Toluene	0.54	0.00	25.57	
14	Benzene	0.59	0.00	25.44	
33	Bromobenzene	0.79	0.00	24.63	
50	Acetonitrile	0.85	0.15	23.31	0.00
101	*t*-Butyl alcohol	0.41	0.67	23.75	−1.31
102	2-Propanol	0.46	0.78	24.13	−0.73
112	1-Propanol	0.51	0.85	24.57	−0.10
104	Ethanol	0.54	0.86	24.63	+0.08
105	Methanol	0.60	0.98	25.71	+1.40
107	Ethylene glycol	0.85	0.92	24.53	+1.01
111	Water	1.09	1.11	24.78	+2.42

a) Solvent numbering is the same in all papers of this series.

calculate this hydrogen bonding effect by,

$$\Delta\Delta\nu(\mathbf{1}-\pi^*) = \nu(\mathbf{1})^{\mathrm{obsd}}_{\max} - \nu(\mathbf{1})^{\mathrm{calcd}}_{\mathrm{Eq.\ 3}}. \qquad (7)$$

Values of $\Delta\Delta\nu(\mathbf{1}-\pi^*)$ for the protic solvents are also assembled in Table 1.

It is seen in the table and the figure that while the net hydrogen bonding effect is essentially *nil* for the very weak HBD solvent acetonitrile (solvent 50), significant displacements from the regression line are observed for the R–OH solvents. For the intermediate strength hydrogen bond donors, *t*-butyl alcohol (101) and 2-propanol (102), the $\Delta\Delta\nu$ terms are negative (shifted bathochromically relative to Eq. 3); for the stronger HBD solvents, methanol (105), ethylene glycol (107), and water (111), $\Delta\Delta\nu$'s are positive (shifted hypsochromically).

While this hints at a complex solvation mechanism, the relationship between $\Delta\Delta\nu(\mathbf{1}-\pi^*)$ and the solvent α values (α being the parameter which measures solvent HBD acidity)[2] is noticeably simple and precise. A plot of $\Delta\Delta\nu(\mathbf{1}-\pi^*)$ against α for the R–OH solvents is shown in Fig. 2. It is seen that linear regression is excellent; the correlation equation is,

$$\Delta\Delta\nu(\mathbf{1}-\pi^*) = (-7.30 + 8.80\alpha) \times 10^3\ \mathrm{cm}^{-1}, \qquad (8)$$

$$n = 7,\ r = 0.989,\ sd = 0.20 \times 10^3\ \mathrm{cm}^{-1}.$$

Equations 3 and 8 can be combined to give the total solvatochromic equation for 4-nitrophenoxide spectra in hydroxylic solvents,

$$\nu(\mathbf{1})_{\max} = (19.41 - 3.99\pi^* + 8.80\alpha) \times 10^3\ \mathrm{cm}^{-1}. \qquad (9)$$

Alternatively the dependence of $\nu(\mathbf{1})_{\max}$ on the solvatochromic parameters may be determined by the method of multiple linear regression analysis. For the seven hydroxylic solvents of Table 1, the multiple parameter least squares fit is given by Eq. 10a.

$$\nu(\mathbf{1})_{\max} = (19.88 - 3.13\pi^* + 7.67\alpha) \times 10^3\ \mathrm{cm}^{-1}, \qquad (10a)$$

$$r = 0.936,\ sd = 0.22 \times 10^3\ \mathrm{cm}^{-1}.$$

If, however, the result for ethylene glycol (whose π^* and α values are relatively less certain) is excluded, the correlation equation becomes,

$$\nu(\mathbf{1})_{\max} = (19.44 - 3.90\pi^* + 8.66\alpha) \times 10^3\ \mathrm{cm}^{-1}, \qquad (10b)$$

$$r = 0.963,\ sd = 0.20 \times 10^3\ \mathrm{cm}^{-1}.$$

The agreement between Eqs. 9 and 10b is surprisingly good if one considers that (a) the *s* values are based on completely different data sets; (b) the π^* values for hydroxylic solvents are somewhat less precise than those for aprotic solvents; and (c) the effects of dipolarity and hydrogen bonding are in different directions and tend to cancel one another, thus narrowing the range of the $\nu(\mathbf{1})_{\max}$ values in the hydroxylic solvents compared with the aprotic solvents. The negative sign of the π^* term indicates that increasing solvent dipolarity/polarizability leads to a red shift; the positive sign of the α term indicates that increasing solvent HBD acidity leads to a blue shift. The similar

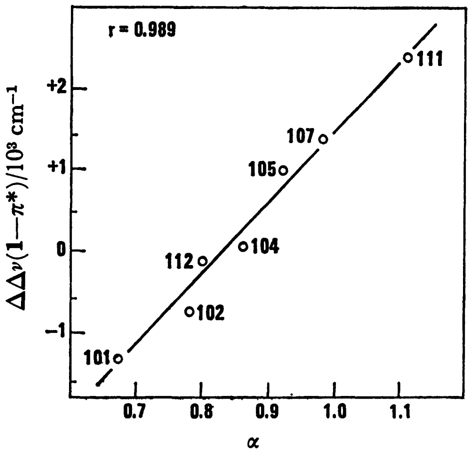


Fig. 2. $\Delta\Delta\nu(\mathbf{1}-\pi^*)$ for hydroxylic solvents plotted against solvent α values.

values of s in Eqs. 3 and 10b imply (perhaps incorrectly or adventitiously, as discussed below) that the dipolarity effects on $\nu(\mathbf{1})_{\max}$ are the same in hydroxylic and non-protonic solvents. There are additional considerations, however, which affect the results.

Specific solvation effects are complicated by the expectation of bonding at two sites. For example, hydrogen bonding to the nitro oxygens[8,9] should stabilize canonical structure **1d** and hence the electronic excited state, and thus lead to a bathochromic shift (as has been demonstrated for *N*,*N*-diethyl-4-nitroaniline).[8] Bonding to the phenoxide oxygen should stabilize structure **1a** and the ground state, and lead to a hypsochromic shift (as mentioned by U. and K.). The phenoxide site being significantly the more basic,[9] the net hypsochromic effect of hydrogen bonding (or other specific solvation)[10] is as expected.

The 7.3×10^3 cm^{-1} difference in the $\nu(\mathbf{1})_0$ values (intercepts) in Eqs. 3 and 10b requires explanation. The $\nu(\mathbf{1})_0$ value represents the regression result in a saturated hydrocarbon environment ($\pi^* = 0$, $\alpha = 0$ for cyclohexane).

We take the difference in $\nu(\mathbf{1})_0$ as implying that the electronic structures of 4-nitrophenoxide in both ground and electronic excited states are different in aprotic and hydroxylic solvents. From the 7.3 10^3 cm^{-1} higher $\nu(\mathbf{1})_0$ in Eq. 3 relative to Eq. 10b, the difference would appear to derive from significant stabilization of the ground state and/or destabilization of the excited state structure in the aprotic solvents relative to the corresponding 4-nitrophenoxide structures in the hydroxylic solvents. An explanation proposed by U. and K. provides an adequate rationale for such an effect.

These workers have pointed out that in aprotic solvents there is strong ion-pairing between the phenoxide anion and the 15-crown-5-bound sodium cation, whereas in hydroxylic solvents ion-pairing is negligible [indeed, the addition of crown ether produced essentially no effect on $\nu(\mathbf{1})_{\max}$ in the hydroxylic solvents]. In the extrapolation of the experimental results of Table 1 back to $\pi^* = 0$ and $\alpha = 0$, such ion-pairing should significantly stabilize the ground state structure of **1** relative to the excited state in the case of the non-protonic solvents, but not in the hydroxylic solvents. Furthermore, 'tighter' ion-pairing with decreasing solvent dipolarity (as well as the decrease in any specific solvation of the nitro substituent)[10] should increase the magnitude of this effect as the π^* values became smaller in the solvents studied experimentally. It should be recognized, however, that if this rationale is correct, the agreement between Eqs. 9 and 10b may be largely adventitious, or possibly regression equation 10a may be more nearly correct.

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