EFFECT OF MEDIUM ON THE ELECTRONIC SPECTRA
OF 2-NITROANILINE DERIVATIVES

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The wavenumbers of the long-wavelength absorption band were measured for nine 4-substituted and 5-substituted derivatives of 2-nitroaniline in the gaseous state and in 13 solvents where only nonspecific solvent–solute interactions can be expected. For the series involving all the solvents used, the solvent effects can be well expressed by an one-parameter equation involving the product of the Born functions of the relative permittivity and of the refractive index of the solvent. For the series involving the nonpolar solvents and the gaseous state only, this equation reduces to an one-parameter equation involving the refractive index Born function squared.
Key words: Solvent effect; Electronic spectra; 2-Nitroanilines.

Solvent effects have been studied extensively over the past two decades, not only with a view to making use of the solvent effects as a tool for studying the mechanisms occurring in solutions, but also within continuing efforts to create a universal and reliable method for evaluation of such effects. In addition to the methods of chemical physics, often referred to as theoretical methods, empirical methods concerned with the macroscopic physical and chemical properties of solvents have also been elaborated. Based on such empirical studies, about 50 sets of solvent characteristics have been developed, from functions of fundamental physical properties of liquids such as the dipole moment, relative permittivity, refractive index, cohesion energy, and other properties, to chemical and spectral methods where the solvent is characterized by how deeply it affects the chemical or spectral properties of solute relative to the effect of a reference solvent, to statistical methods where the solvent characteristics are calculated from more or less extensive sets of physical, chemical and spectral properties of solutions using statistical approaches (for reviews see, e.g., refs[1–5]). Several methods characterizing the medium primarily by the dielectric properties of the solvent have been developed to evaluate the effect of medium on the electronic spectra of solutes. All of the equations suggested involve two terms at least, which are various functions of the relative permittivity and refractive index of the solvent[2,5–7]. The efficiency of such methods has been tested[7–9] with respect to both the correlation characteristics and the calculated dipole moments of solute molecules in the excited state. Comparison studies[8,9] have demon-

strated that the effect of nonspecific interactions on the electronic spectra of solutes are best described by an one-parameter equation involving the product of the Born functions of the relative permittivity (ε_r) and of the refractive index (n) of the solvent, viz.

$$\tilde{\nu} = A + B\,(1 - 1/\varepsilon_r)\,(1 - 1/n^2)\ . \tag{1}$$

A drawback of the majority of such sets of solvent characteristics is in the fact that they have been set up for the conventional range of solvents, usually from hexane over halogen derivatives of hydrocarbons, ethers, and esters to the most "polar" solvents as are dimethyl sulfoxide, alcohols, and water. Actually, however, physical characteristics such as the various relative permittivity functions vary over the gaseous state–cyclohexane range to an extent which is mostly comparable to that over the cyclohexane–water range. For instance, the Born function $(1 - 1/\varepsilon_r)$ is 0.00 for the gaseous state, 0.50 for cyclohexane, and 0.99 for water; the corresponding Onsager function values are 0.00, 0.20, and 0.48, respectively. The volume of gaseous state data is richest in papers dealing with the effect of medium on vibrational spectra[2,3]. In chemical equilibrium and reactivity studies, such data are very scarce, and about 15 values can be extracted from papers dealing with electronic spectroscopy.

The present work is concerned with the electronic spectra of 9 derivatives of 2-nitroaniline in the gaseous state and in a series of solvents where nonspecific solvent–solute interactions only are expected[1], with a view to extending the number of sets containing electronic spectral data of compounds in the gaseous state.

EXPERIMENTAL

The solvents, except for diiodomethane, were purified by distillation, and the fractions boiling at the tabulated temperatures were used for the measurement. The 2-nitroaniline derivatives were available in the Laboratory, and their identity and purity were checked by elemental analysis.

Electronic spectra were measured on a PYE UNICAM 8750 UV/VIS spectrophotometer using fused silica cells 5 mm optical pathway (1 mm for diiodomethane and carbon disulfide solutions). Gas state measurements were performed in fused silica cells 10 cm pathway at 80–100 °C.

RESULTS AND DISCUSSION

The wavenumbers of the longest-wavelength absorption bands of the 4-substituted and 5-substituted 2-nitroanilines in the gaseous state and in 13 solvents are given in Table I. All of the derivatives exhibit a marked bathochromic effect over the 29 000 to 22 000 cm^{-1} range. The experimental data were correlated by the Born functions in the form of the one-parameter equation (1) and the two-parameter equation (2) involving separately the Born functions of relative permittivity and of the refractive index:

$$\tilde{v} = A' + B\,(1 - 1/\varepsilon_r) + C\,(1 - 1/n^2) \quad . \tag{2}$$

As in the previous comparison studies[8,9], the equation containing a single parameter (Eq. (1)) is better suited to the correlation of the experimental data than the two-parameter equation (Eq. (2)). A comparison of the correlation characteristics is presented in Table II. The correlation coefficients are invariably higher, by 0.02 at least, and the standard deviations are considerably lower for Eq. (1) than for Eq. (2).

A higher efficiency of the product term as compared to the sum of the terms involving the separate relative permittivity and refractive index functions can also be demonstrated by analysis of the data set pertaining to nonpolar solvents where $\varepsilon_r = n^2$ (solvents No. 2–9 in Table I) and to the gaseous state. In this case, Eq. (1) reduces to the dependence of the absorption wavenumber on the refractive index Born function squared, while the two-parameter equation (2), as well as other two-parameter equations, re-

TABLE I
Effect of medium on the wavenumbers of the longest-wavelength absorption bands of 2-nitroaniline derivatives

No.	Medium	$\tilde{v} \cdot 10^{-3}$, cm^{-1}								
		4-CH$_3$	4-OCH$_3$	5-OCH$_3$	4-OC$_2$H$_5$	4-F	4-Cl	5-Cl	4-Br	4-I
1	Gas state	27.38	25.93	29.00	25.83	27.23	27.20	28.41	27.06	26.98
2	Pentane	25.79	24.32	27.53	24.27	25.77	25.77	27.17	25.77	25.54
3	Cyclopentane	25.64	24.18	27.35	24.08	25.61	25.61	26.82	25.61	25.41
4	Hexane	25.72	24.27	27.47	24.22	25.69	25.70	26.94	25.72	25.51
5	Cyclohexane	25.61	24.13	27.29	24.04	25.51	25.51	26.80	25.51	25.41
6	Heptane	25.72	24.18	27.29	24.13	25.61	25.61	26.93	25.61	25.46
7	Carbon tetrachloride	25.15	23.74	26.88	23.63	25.20	25.25	26.48	25.20	25.05
8	Tetrachloroethylene	25.20	23.72	26.88	23.63	25.20	25.25	26.46	25.21	25.01
9	Carbon disulfide	24.65	23.11	26.18	23.11	24.80	24.85	26.06	24.75	24.54
10	Trichloroethylene	24.90	23.41	26.60	23.36	24.95	24.95	26.23	24.95	24.75
11	Dichloromethane	24.41	22.98	26.05	22.81	24.46	24.51	25.58	24.51	24.37
12	1,1,2,2-Tetrachloro-ethane	24.08	22.77	25.83	22.64	24.28	24.37	25.51	24.32	24.08
13	Dibromomethane	24.04	22.69	25.80	22.60	24.27	24.27	25.51	24.27	24.04
14	Diiodomethane	23.67	22.39	25.40	22.28	23.81	23.95	25.16	24.07	23.70

Results of regression analysis of experimental data by using Eqs (*1*)–(*4*) (equation coefficients *A*–*C*, correlation coefficients *R*, standard deviations *s*)

Parameter	4-CH$_3$	4-OCH$_3$	5-OCH$_3$	4-OC$_2$H$_5$	4-F	4-Cl	5-Cl	4-Br	4-I
				Eq. (*1*)					
A^a	27.14	25.71	29.20	25.73	27.14	27.03	28.34	26.94	26.72
sA^a	0.06	0.08	0.09	0.06	0.06	0.05	0.06	0.05	0.06
$-B$	6.52	6.23	6.35	6.29	5.83	5.61	5.82	5.40	5.70
sB	0.18	0.22	0.24	0.18	0.18	0.20	0.30	0.15	0.20
R	0.996	0.993	0.992	0.995	0.995	0.995	0.996	0.996	0.995
s^a	0.09	0.11	0.13	0.10	0.10	0.08	0.08	0.07	0.09
				Eq. (*2*)					
A^a	27.72	26.23	28.95	26.11	27.55	27.38	28.60	27.32	27.09
sA^a	0.24	0.21	0.24	0.21	0.20	0.18	0.20	0.18	0.14
$-B$	3.30	2.99	3.81	3.18	2.88	2.82	3.16	2.80	2.81
sB	0.53	0.45	0.46	0.45	0.44	0.38	0.43	0.39	0.31
$-C$	1.13	1.43	1.07	1.15	1.17	1.07	0.67	0.87	0.85
sC	0.80	0.69	0.16	0.68	0.66	0.58	0.65	0.59	0.48
R	0.969	0.975	0.970	0.976	0.973	0.978	0.974	0.976	0.984
s^a	0.26	0.22	0.27	0.22	0.21	0.19	0.19	0.19	0.15
				Eq. (*3*)					
A^a	27.34	25.90	29.03	25.70	27.15	27.11	28.38	27.04	26.94
sA^a	0.08	0.06	0.07	0.06	0.08	0.08	0.07	0.05	0.06
$-B$	7.07	7.22	7.16	7.08	6.39	6.16	6.21	6.01	6.30
sB	0.31	0.25	0.29	0.25	0.29	0.29	0.26	0.20	0.23
R	0.993	0.996	0.995	0.996	0.993	0.992	0.994	0.996	0.995
s^a	0.09	0.07	0.08	0.07	0.09	0.09	0.08	0.06	0.07
				Eq. (*4*)					
A^a	27.51	26.06	29.16	25.96	27.32	27.28	28.52	27.17	27.09
sA^a	0.19	0.20	0.24	0.19	0.13	0.12	0.17	0.16	0.16
$-B$	4.04	4.11	4.02	4.04	3.70	3.58	3.55	3.42	3.61
sB	0.39	0.40	0.48	0.38	0.28	0.24	0.34	0.34	0.33
R	0.968	0.969	0.953	0.971	0.981	0.985	0.969	0.968	0.973
s^a	0.20	0.20	0.25	0.19	0.14	0.12	0.17	0.17	0.16

^{a} In 10^{-3} cm^{-1}.

duces to an one-parameter dependence of the wavenumber on the 1st power of the corresponding refractive index function. Hence, the dependences related to Eqs (*1*) and (*2*) are Eqs (*3*) and (*4*), respectively:

$$\tilde{v} = A + B \, (1 - 1/n^2)^2 \ . \tag{3}$$

$$\tilde{v} = A + B \, (1 - 1/n^2) \ . \tag{4}$$

The efficiency of Eqs (*3*) and (*4*) is also compared in Table II. Also in this case of sets of nonpolar solvents solely, the correlation characteristics are appreciably more favourable when using the dependence of the wavenumber on the refractive index Born function squared than when using the dependence on the 1st power of that function.

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