EVALUATION OF SOLVENT EFFECTS IN ELECTRONIC SPECTRA

Vojtěch BEKÁREK

Faculty of Natural Sciences,
Palacký University, 771 46 Olomouc

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Applicability of the Buckingham cross-term $f(D, n^2) = (D - 1)(n^2 - 1)/(2D + 1)(2n^2 + 1)$ for evaluation of solvent shifts has been tested using 12 original and 4 published data sets concerning solvent effects in electronic spectra. The results are compared with correlation of the same data with the Bakshiev equation. Influence of the cross-term on the solvent shifts is dominant with the systems showing no direction change of the molecular dipole moment during excitation. Mutual dependence has been found between the cross-term and the Taft solvent factors π^* at the 90% significance level.

During the past 25 years considerable attention has been paid to problems of quantitative evaluation of influence of medium on electronic spectra, which was due both to analytical importance of the problems and to expected possibility of assessment of the dipole moment of excited molecules (solvatochromic method) and evaluation of the solvation process (estimation of radii of the Onsager solvation cavity). Both theoretical and empirical methods were proposed for evaluation of solvent effects on electronic spectra, the former ones being based on classic or quantum-mechanical models. Their results are expressed in one- or multi-parameter relations giving explicitely the dependence of the solvent shifts on relative permittivity and refractive index of the medium. A summary of the problems of determination of dipole moments of excited molecules is given by Koutek[1]. The empirical methods express the influence of medium on electronic spectra by solvent indexes which are related to the solvent shifts by one-parameter linear relations. To the best known ones belong the solvent indexes of Kosower[2], Brownstein[3], and especially the recent solvent indexes π^* of Taft[4-8]. Furthermore it was shown[9] that these π^* indexes can be applied to description of solvent effects in IR spectroscopy, which indicates similar influence of medium on both electronic and IR spectra. In the field of IR spectroscopy, Buckingham[10] derived a power series for evaluation of solvent effects on position of the absorption bands, in which the only characteristics of the medium are refractive index (n) and relative permittivity (D) of the solvent. On the basis of examination of a large number of data[11,12] we showed the cross-term of the Buckingham power series to have dominant influence in evaluation of effects of medium, this term (in an one-parameter equation) being practically sufficient for evaluation of solvent effects

in IR spectra. We also found a very good correlation between this cross-term and the empirical solvent parameters suggested by Allerhand and Schleyer[13] and Bellamy[14] for evaluation of solvent effects in IR spectra.

The aim of this communication was to test the applicability of the Buckingham cross-term for correlation of the solvent-induced shifts of absorption bands in electronic spectra, to compare this correlation with that using the Bakhshiev equation[15], and to evaluate the relation between the Taft solvent indexes π^* and the Buckingham cross-term.

EXPERIMENTAL

The spectra were measured with a Unicam SP 1800 apparatus in 0·01 to 1 cm cells (concentrations 10^{-5}M to 10^{-3}M) according to absorption of the solvents used and solubility of the substances studied. No concentration dependence of position of the studied maxima was observed in the given concentration range. The solvents were the same as in refs[11,12].

RESULTS AND DISCUSSION

The studied absorption maxima measured in 12 solvents are given in Table I. The following model substances were chosen: 2-nitroaniline (*I*), 4-nitroaniline (*II*), 3-nitroaniline (*III*), 4-dimethylaminobenzonitrile (*IV*), 4-aminoacetophenone (*V*), 2-chloroaniline (*VI*), 2-nitrophenol (*VII*), 4-nitrophenol (*VIII*), 3-nitrophenol (*IX*), salicylaldehyde (*X*), phenoxazin-3-one (*XI*), and 2-nitroso-1-naphthol (*XIII*). For the present study we chose the solvents for which minimum specific interactions with the compounds studied could be expected. Also we did not use too polar solvents, because, due to the saturation effects, they need not fulfil linear dependence between the dipole moment induced in the solvent and the field intensity which brings about this moment, which is however, one of the starting presumptions of all theoretical methods for evaluation of the solvent effects.

The experimental data were correlated with Eq. (*1*) and with the Bakhshiev equation (*2*) (ref.[13]) in the form recommended in ref.[1]:

$$\lambda = \mathrm{A} + \mathrm{B}(D-1)(n^2-1)/(2D+1)(2n^2+1) + \mathrm{C}(n^2-1)/(2n^2+1)\,. \quad (1)$$

$$\lambda = \mathrm{A}' + \mathrm{B}'[(D-1)/(D+2) - (n^2-1)/(n^2+2)](2n^2+1)/(n^2+2) + \mathrm{C}'(n^2-1)/(n^2+2)\,. \quad (2)$$

The regression parameters A, B, C, A', B', C' are given in Table II along with the correlation characteristics (the correlation coefficient R, the partial correlation coefficients $r(\lambda - \mathrm{f}(D, n^2))$ and $r(\lambda - \mathrm{f}(n^2))$, and the Fischer criterion F). Besides these experimental data of ours we carried out the regression analysis with Eqs (*1*) and (*2*) for four sets published by Taft and coworkers[4-6] *viz.* 4-nitro-1-methoxybenzene, N,N-

TABLE I

Influence of Medium on Absorption Maxima of the Studied Systems

Solvent	$f(\varepsilon, n^2)$	$f(n^2)$	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*
Gas	0·000	0·000	—	—	—	—	—	286·0	—	—	—	321·0	—	—
Perfluorohexane	0·018	0·134	—	—	—	—	—	—	—	—	—	324·5	—	—
n-Pentane	0·031	0·176	374·5	315·5	344·0	280·0	283·0	290·0	345·5	282·0	307·0	327·5	426·0	417·0
n-Hexane	0·034	0·185	375·5	319·0	345·0	280·5	285·0	290·5	346·5	284·0	310·0	328·0	427·0	417·0
n-Heptane	0·037	0·192	376·5	321·0	346·0	281·0	285·0	291·0	347·0	286·0	309·0	328·5	427·0	418·5
Cyclohexane	0·041	0·204	377·0	321·5	347·5	282·0	288·0	291·0	347·5	286·0	309·0	328·5	427·0	418·0
Tetrachloromethane	0·048	0·214	383·0	330·0	352·5	290·5	293·5	293·5	349·5	290·0	317·0	329·5	436·5	420·0
Tetrachlorethylene	0·053	0·228	382·5	—	354·5	287·5	294·0	293·0	352·0	—	—	330·0	436·5	—
Carbon disulphide	0·068	0·261	391·5	342·5	—	—	—	—	—	—	—	—	444·0	428·0
1,1,2-Trichlorethylene	0·068	0·220	389·5	341·0	358·0	290·5	296·5	292·0	353·0	298·0	320·0	329·5	439·0	—
Dichloromethane	0·085	0·202	396·0	349·5	363·0	294·0	298·5	292·0	354·5	300·5	322·5	328·5	442·5	421·5
1,2-Dichlorethane	0·090	0·210	397·0	353·0	365·5	293·5	299·5	292·0	354·5	302·0	324·0	329·0	442·0	420·0
Dibromomethane	0·096	0·239	400·0	355·0	368·0	300·0	303·5	293·5	357·5	306·0	327·0	331·5	448·0	427·0
Diiodomethane	0·106	0·287	406·5	—	—	—	—	—	—	—	—	—	462·0	435·0

TABLE II

Results of Regression Analysis of Experimental Data with Equations (*1*) and (*2*)

Parameter	*I*	*II*	*III*	*IV*	*V*	*VI*	*VII*	*VIII*	*IX*	*X*	*XI*	*XII*
A [nm]	356·1	289·6	323·3	254·9	285·7	254·9	330·7	260·1	285·9	320·4	389·7	388·9
B [nm]	381·5	577·4	328·8	211·7	13·2	209·5	130·6	299·9	238·6	12·5	250·6	32·9
C [nm]	33·6	50·7	57·6	100·1	26·2	123·4	59·9	73·3	79·3	37·8	149·5	143·9
R	0·997	0·996	0·997	0·966	0·949	0·990	0·993	0·996	0·979	0·979	0·982	0·975
F	637·1	458·7	640·2	49·4	36·2	176·8	260·7	369·9	69·9	101·7	121·9	68·6
$r(\lambda - f(D, n^2))$	0·994	0·994	0·993	0·943	0·780	0·957	0·971	0·991	0·970	0·787	0·931	0·785
$r(\lambda - f(n^2))$	0·758	0·662	0·735	0·785	0·941	0·826	0·803	0·813	0·817	0·975	0·883	0·969
A′ [nm]	345·0	275·7	314·2	251·0	285·7	252·6	328·5	251·2	279·4	320·5	389·5	395·1
B′ [nm]	28·72	43·30	24·10	15·24	0·54	15·30	9·48	21·21	16·87	0·202	18·31	2·33
C′ [nm]	132·3	189·9	135·9	129·9	23·4	141·8	78·04	143·5	128·7	32·26	161·1	94·92
R	0·994	0·994	0·998	0·967	0·956	0·991	0·993	0·992	0·979	0·986	0·981	0·980
F	400·6	311·0	826·4	51·1	42·1	192·7	239·7	191·0	71·3	158·0	115·9	85·8

-diethyl-4-nitroaniline, N,N-dimethyl-2-nitro-4-toluidine and N,N-dimethyl-2-nitroaniline. The regression analysis results are given in Table III. The correlation characteristics show that Eq. (*1*) fits the experimental data very well and in similar extent as the Bakhshiev equation. It is interesting to examine relative magnitude of effects of the cross-term $f(D, n^2)$ and the Bayliss[10] term $f(n^2)$ of Eq. (*1*) in evaluation of the solvent shifts. The former term is dominant with the systems containing strong electron-donor and electron-acceptor groups, being highest in the cases when these groups are mutually in *para* positions. In these cases the dipole moments of solute molecule in the ground and the excited states are obviously colinear, as it is the case with valence vibrations of the bonds studied by IR spectroscopy where simple linear relation between the solvent shift and the cross-term is obeyed. As these compound types served as primary indicators for determination of the π^* solvent indexes, a linear relation between these π^* factors and the cross-term values can be expected. This correlation was carried out for all the solvents for which these π^* factors were proposed (except for water and alcohols); the correlation has the following form:

$$\pi^* = 14{\cdot}52\, f(D, n^2) - 0{\cdot}514\,, \quad R = 0{\cdot}904\,, \quad F = 205\,. \tag{3}$$

The correlation is significant at the 90% probability level. The value $-0{\cdot}514$ represents the π^* index for gaseous state. Considerably high significance is obtained

TABLE III

Results of Regression Analysis of Some Published Systems[3-5] using Equations (*1*) and (*2*)

Parameter	4-Nitro--1-methoxybenzene	N,N-Diethyl--4-nitroaniline	N,N-Dimethyl--2-nitroaniline	N,N-Dimethyl--2-nitro--4-toluidine
A [cm^{-1}]	36 820	30 150	27 810	27 100
B [cm^{-1}]	−30 400	−38 400	−24 950	−25 880
C [cm^{-1}]	− 8 600	7 560	− 8 890	− 7 760
R	0·975	0·951	0·976	0·963
F	146·3	98·7	109·9	69·4
$r(\bar{\nu} - f(D, n^2))$	0·964	0·941	0·956	0·952
$r(\bar{\nu} - f(n^2))$	0·535	0·403	0·490	0·554
A′ [cm^{-1}]	37 130	30 980	28 290	27 450
B′ [cm^{-1}]	−19 300	− 2 560	− 1 710	− 1 780
C′ [cm^{-1}]	−13 570	−15 980	−13 170	−11 900
R	0·980	0·953	0·979	0·958
F	184·8	105·0	129·2	61·2
n	18	24	14	14

when this correlation is carried out with 28 so called selected[18] solvents:

$$\pi^* = 14{\cdot}90\, f(D, n^2) - 0{\cdot}578\,, \quad R = 0{\cdot}980\,, \quad F = 527\,. \qquad (4)$$

In the case of the studied absorption bands of salicylaldehyde (*X*), 4-aminoacetophenone (*V*) and 2-nitroso-1-naphthol (*XII*) the solvent shifts are predominantly affected by the Bayliss term $f(n^2)$. As the said compounds are polar, it cannot be presumed that there are no dipole–dipole interactions between them and the solvent molecules (similar behaviour is encountered with a great number of other compounds as *e.g.* azocompounds, chlorophyll[17]). More likely the reason is in the fact that the solvent molecules are not oriented around the solute molecule due to the changes taking place in the direction of dipole moment of the molecule in the course of its excitation. Electronic and atomic polarization of the solvent molecules and, hence, also the effect of the corresponding reaction field on the energy levels of the solute molecule are not modified in the way encountered with the molecules in which no change of the dipole moment direction takes place during excitation. The significance of the cross-term and the Bayliss $f(n^2)$ term of Eq. (*1*) could thus serve as a measure of colinearity of the dipole moments of the molecule in the ground and the excited states. Out of the studied compounds, the obviously significant effect of the both terms is encountered in the case of phenoxazin-3-one. This non-colinearity of the dipole moments of the molecule in its ground and excited states results in inapplicability of the solvatochromic method for determination of the dipole moments of these compounds in their excited states. In these cases it is also impossible to use the Taft π^* indexes for evaluation of effect of medium on the solvent shifts, whereby versatility of these indexes is considerably reduced.

REFERENCES

1. Koutek B.: This Journal *43*, 2368 (1978).
2. Kosower E. M.: J. Amer. Chem. Soc. *80*, 3253 (1958).
3. Brownstein S.: Can. J. Chem. *38*, 1590 (1960).
4. Kamlet M. J., Taft R. W.: J. Amer. Chem. Soc. *98*, 377 (1976).
5. Taft R. K., Kamlet M. J.: J. Amer. Chem. Soc. *98*, 2886 (1976).
6. Yokoyama T., Taft R. W., Kamlet M. J.: J. Amer. Chem. Soc. *98*, 3233 (1976).
7. Kamlet M. J., Abboud J. L., Taft R. W.: J. Amer. Chem. Soc. *99*, 6027 (1977).
8. Kamlet M. J., Taft R. W.: J. Chem. Soc., Perkin Trans. 2 *1979*, 349.
9. Kamlet M. J., Taft R. W.: J. Chem. Soc., Perkin Trans. 2 *1979*, 337.
10. Buckingham A. D.: Proc. Roy. Soc. A *248*, 169 (1958).
11. Bekárek V., Mikulecká A.: This Journal *43*, 2879 (1978).
12. Bekárek V., Knopová M.: Acta Univ. Palacki. Olomuc., Fac. Rerum Natur., in press.
13. Allerhand A., Schleyer P. R.: J. Amer. Chem. Soc. *85*, 371 (1963).
14. Bellamy L. J., Hallam H. E., Williams R. L.: Trans. Faraday Soc. *54*, 1120 (1958).

15. Bakhshiev N. G.: Opt. Spektrosk. *10*, 717 (1961).
16. Bayliss N. S.: J. Chem. Phys. *18*, 292 (1950).
17. Seely G. R., Jensen R. G.: Spectrochim. Acta *21*, 1835 (1965).
18. Abboud J. L., Kamlet M. J., Taft R. W.: J. Amer. Chem. Soc. *99*, 8325 (1977).

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