

## A CONTRIBUTION TO EVALUATION OF EFFECTS OF MEDIUM ON ELECTRONIC SPECTRA

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Efficiency has been compared of the Bayliss-McRae-Ooshika, Bakhshiev, and cross term methods in evaluation of the effect of medium on electronic spectra of nine indicators of polarity of medium using also the data obtained in gas phase and in perfluorinated hydrocarbons.

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Evaluation of the effect of medium on electronic spectra continues to represent a living and topical problem due to necessity of determination of the dipole moment of molecules in the excited state and to the problems connected with the empirical methods of evaluation of the effects of medium on chemical processes. So far a large number of methods have been suggested for evaluation of the effect of medium on electronic spectra, all of them representing functions of different degree of complexity, involving the relative permittivity and refractive index of the medium, and resulting from differently detailed starting models. Applicability of these methods has been tested with regard to both the agreement between experimental and calculated values and the point of view of correctness of the dipole moments so obtained for molecules in the excited state<sup>1-4</sup>. These tests, however, are carried out by various authors using different selected groups of solvents, which (along with the fact that the experimental data used are not usually given and are taken from various sources) makes the conclusions uncertain and their comparison difficult. Recently, wavenumbers of transitions have been obtained for some compounds in gas phase and in perfluorinated hydrocarbons<sup>5,6</sup>, which extended the scale of experimental data almost to the double and increased the contribution of the functions of refractive index as much as three times depending on their forms.

The aim of the present communication is to compare the applicability of the Bayliss-McRae-Ooshika method<sup>7</sup>, Bakhshiev method<sup>8</sup>, and the cross term method<sup>1</sup> to evaluation of the effect of medium on electronic spectra also in gas phase and in perfluorinated hydrocarbons.

### EXPERIMENTAL

Most data were taken from refs<sup>1,5,6,9,10</sup>. Measured were the electronic spectra of 2-nitroaniline and N,N-dimethylamino-4-nitrosobenzene in gas phase and in several media for which no published data were available. The measurements in gas phase were carried out in 100 mm quartz cells at the temperatures of 60 and 90°C using a Unicam SP 1 800 apparatus. All the data used in the correlations are given in Table I.

TABLE I  
Effect of medium on position of lines in electronic spectra of the compounds studied ( $10^3 \text{ cm}^{-1}$ )

Solvent	Compound								
	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>	<i>IX</i>
Gas phase	28·30	27·30	36·90	34·48	30·39	27·57	37·31	28·20	30·90
Perfluorohexane	27·17	—	—	—	—	26·32	—	—	—
Perfluoroheptane	—	6·292	35·15	32·29	—	—	—	27·23	29·64
Perfluorooctane	—	26·37	35·15	32·29	—	—	—	27·24	29·67
Perfluoromethyldecaline	—	26·27	34·94	32·20	—	—	—	27·10	29·32
n-Hexane	26·35	25·84	34·31	31·35	27·71	25·48	35·21	26·61	28·98
n-Pentane	26·46	25·91	—	31·67	—	26·61	35·46	26·70	29·07
n-Heptane	26·25	25·76	—	31·20	—	25·45	34·97	26·56	28·92
Cyclohexane	26·11	25·71	34·13	31·07	27·40	25·32	34·97	26·50	28·80
Tetrachloromethane	25·61	25·19	33·56	30·32	26·70	24·88	34·48	26·05	28·41
Tetrachloroethylene	25·58	25·25	—	30·40	—	—	—	26·11	28·50
Trichloroethylene	25·06	24·94	—	29·33	25·76	—	33·56	25·67	27·93
Carbon disulphide	24·88	24·75	—	29·20	—	24·18	—	25·52	—
Diethyl ether	25·41	—	33·45	—	26·52	25·06	—	—	—
Tetrahydrofuran	24·69	—	32·79	—	25·61	24·39	—	—	—
n-Octane	—	25·74	—	31·28	—	—	—	26·51	28·92
n-Nonane	—	25·70	—	—	—	—	—	—	—
n-Decane	—	25·71	—	31·22	—	—	—	26·50	28·90
Methylcyclohexane	—	25·65	—	31·08	—	—	—	26·42	28·84
Dichloromethane	24·39	24·36	32·25	28·61	24·96	23·87	33·28	25·25	27·55
1,2-Dichloroethane	24·33	24·45	—	28·33	25·06	23·87	33·11	25·19	27·36
Dibromomethane	24·07	—	—	28·17	—	23·53	32·70	25·00	27·17
Diiodomethane	23·64	—	—	—	—	22·91	—	24·60	—
Chloroform	—	—	—	—	25·08	—	—	—	—
Ethyl acetate	25·03	—	32·79	—	25·74	24·48	—	—	—
Ethyl formiate	24·94	—	—	—	—	24·33	—	—	—
Triethylamine	—	—	—	—	27·14	—	—	—	—
Acetone	24·57	—	—	—	25·22	24·01	—	—	—
Isobutylmethylketone	24·69	—	—	—	—	24·24	—	—	—
Acetonitrile	24·45	—	32·47	—	—	23·75	—	—	—
Cyclopentanone	24·33	—	—	—	—	23·87	—	—	—
Nitromethane	24·18	—	—	—	—	—	—	—	—
Dimethylformamide	24·10	—	32·05	—	24·66	23·64	—	—	—
Butyrolactone	—	—	31·95	—	24·60	—	—	—	—
N-Methylpyrrolidone	—	—	31·90	—	24·60	—	—	—	—
Hexamethylphosphor- diamide	—	—	31·90	—	24·75	—	—	—	—
Di-n-butyl ether	—	—	33·56	—	26·85	—	—	—	—
Dimethylacetamide	—	—	32·05	—	24·75	—	—	—	—
Butanone	—	—	33·56	—	25·28	—	—	—	—
Dimethyl sulphoxide	23·81	—	31·70	—	24·30	23·20	—	—	—

## RESULTS AND DISCUSSION

The wavenumbers of transitions of the nine indicators investigated are given in Table I. The following compounds were used: 3-nitro-N,N-dimethylaniline (*I*), 2-nitro-4-toluidine (*II*), 4-nitroanisole (*III*), 4-nitroaniline (*IV*), 4-nitro-N,N-diethylaniline (*V*), 4-nitroso-N,N-dimethylaniline (*VI*), 4-nitrophenol (*VII*), 2-nitroaniline (*VIII*), and 3-nitroaniline (*IX*). The equations used for evaluation of the effect of medium on the position of spectral lines of the above-mentioned compounds have the following forms:

the Bakhshiev equation:

$$\tilde{\nu} = A + B \left( \frac{2n^2 + 1}{n^2 + 2} \right)^2 \cdot \left( \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + C \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

the Bayliss-McRae-Ooshika equation:

$$\tilde{\nu} = A + B \left( \frac{D - 1}{D + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + C \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

the cross term equation:

$$\tilde{\nu} = A + B \frac{(D - 1)(n^2 - 1)}{(2D + 1)(2n^2 + 1)} + C \frac{n^2 - 1}{2n^2 + 1} \quad (3)$$

The above-mentioned equations were used for the testing of applicability for the following reasons. The Bakhshiev equation was found to be the most suitable for determination of the dipole moment of molecules in the excited state by solvatochromic methods<sup>2</sup>, Abboud, Kamlet and Taft<sup>7</sup> successfully used the Bayliss-McRae-Ooshika equation for interpretation of the  $\pi^*$  parameters of polarity, and the cross term equation proved efficient in evaluation of the effects of medium on electronic and vibrational spectra<sup>1,9</sup>, it was used for interpretation of the  $\pi^*$  parameters of polarity<sup>11</sup> and represented the starting point for establishing of the  $\pi_n^*$  parameters<sup>12,13</sup>. All the equations include the term  $f(n^2) = (n^2 - 1)/(2n^2 + 1)$ . The original Bakhshiev equation contains four terms, three of them being various functions of the refractive index only. Contraction of these three functions into a single one was suggested<sup>2</sup> with the aim of simplification and with respect to mutual correlation of these functions. The second term of the equations used contains besides the refractive index also the relative permittivity of the medium. Values of all these functions are given in Table II.

For this study we used the results of measurements obtained in the solvents which show no specific interactions with the compound measured. Hence, omitted were the data on effects of amphiprotic solvents and (in the cases of the indicators with

TABLE II

Values of the functions of refractive index and relative permittivity in the correlation equations used for the individual solvents

Solvent	$f(n^2)$	$f(D, n^2)$		
		Bakhshiev	B-R-O	cross term
Gas phase	0.000	0.0000	0.000	0.0000
Perfluorohexane	0.134	0.0408	0.0509	0.0214
Perfluoroheptane	0.140	0.0689	0.0509	0.0236
Perfluorooctane	0.146	0.0862	0.0629	0.0263
Perfluoromethyldecane	0.162	0.0638	0.0447	0.0313
n-Hexane	0.185	0.0071	0.	0.0348
n-Pentane	0.180	-0.0010	0.	0.0324
n-Heptane	0.191	-0.0005	0.	0.0365
Cyclohexane	0.204	-0.0032	0.	0.0414
Tetrachloromethane	0.216	0.0277	0.0170	0.0488
Tetrachloroethylene	0.230	0.0074	0.	0.0531
Trichloroethylene	0.221	0.2678	0.1624	0.0683
Carbon disulphide	0.260	-0.0164	-0.0090	0.0679
Diethyl ether	0.178	0.4591	0.3103	0.0614
Tetrahydrofuran	0.198	0.6750	0.4408	0.0796
n-Octane	0.193	0.0000	0.	0.0374
n-Nonane	0.197	-0.0006	0.	0.0386
n-Decane	0.199	0.0000	0.	0.0396
Methylcyclohexane	0.204	-0.0008	0.	0.0412
Dichloromethane	0.202	0.7405	0.4712	0.0848
1,2-Dichloroethane	0.200	0.7927	0.5075	0.0862
Dibromomethane	0.239	0.6221	0.3599	0.0963
Diiodomethane	0.287	0.3680	0.1871	0.1065
Chloroform	0.209	0.4604	0.2870	0.0744
Ethyl acetate	0.185	0.6003	0.3984	0.0712
Ethyl formate	0.182	0.6727	0.4504	0.0732
Acetone	0.180	0.9646	0.6479	0.0837
Triethylamine	0.194	0.1231	0.0799	0.0471
Isobutylmethylketone	0.194	0.8633	0.5613	0.0862
Acetonitrile	0.174	1.0455	0.7135	0.0835
Cyclopentanone	0.208	0.8674	0.5447	0.0926
Nitromethane	0.188	1.0533	0.6947	0.0903
Dimethylformamide	0.205	1.0516	0.6651	0.0984
Butyrolactone	0.207	1.0617	0.6660	0.0972
N-Methylpyrrolidone	0.218	1.0393	0.6338	0.1042
Hexamethylphosphortriamide	0.214	1.0292	0.6339	0.1019
Di-n-butyl ether	0.194	0.2561	0.1675	0.0561
Dimethylacetamide	0.205	1.0552	0.6633	0.0994
Butanone	0.188	0.9436	0.6228	0.0867
Dimethyl sulphoxide	0.220	1.0833	0.6557	0.1069

active hydrogen atom) on electron-donor solvents. Moreover, we did not include the spectra measured in aromatic solvents and dioxane. Included were, of course, also the data on the effect of medium in polyhalogenated solvents.

Table III presents the results of the correlations of the experimental data by Eqs (1)–(3). The Table gives the regression coefficients  $A$ ,  $B$ ,  $C$ , the correlation coefficient

TABLE III

Results of regression analysis of experimental data by the Bakhshiev (B), Bayliss–McRae–Ooshika (BMO), and cross term (CT) equations

Compound (number of solvents)	Equation type	Parameter					
		$A$	$-B$	$-C$	$R$	$\sigma$	$r$
I (25)	B	28.76	1.81	14.09	0.984	0.22	—
	BMO	28.85	2.76	14.63	0.979	0.23	—
	CT	28.21	35.85	3.24	0.995	0.11	0.989
II (18)	B	27.65	1.58	9.98	0.967	0.18	—
	BMO	27.66	2.46	10.03	0.965	0.19	—
	CT	27.37	27.90	2.79	0.991	0.10	0.981
III (22)	B	37.20	1.94	15.85	0.984	0.22	—
	BMO	37.25	3.03	16.12	0.983	0.25	—
	CT	36.93	36.14	6.91	0.993	0.17	0.979
IV (18)	B	35.09	3.35	20.22	0.979	0.33	—
	BMO	35.13	5.32	20.48	0.978	0.24	—
	CT	34.48	54.95	5.78	0.994	0.17	0.985
V (21)	B	30.48	2.31	16.80	0.981	0.28	—
	BMO	30.52	3.65	17.06	0.981	0.29	—
	CT	30.35	44.74	6.42	0.988	0.23	0.977
VI (22)	B	28.00	1.54	14.06	0.981	0.21	—
	BMO	28.07	2.36	14.43	0.977	0.23	—
	CT	27.55	29.70	5.17	0.990	0.15	0.973
VII (10)	B	37.44	2.39	12.78	0.987	0.23	—
	BMO	37.46	3.77	12.97	0.984	0.24	—
	CT	37.32	38.28	4.31	0.997	0.11	0.987
VIII (19)	B	18.66	2.62	11.10	0.975	0.20	—
	BMO	28.70	2.56	11.39	0.971	0.21	—
	CT	28.25	26.00	3.53	0.993	0.11	0.982
IX (17)	B	31.14	1.81	11.40	0.986	0.16	—
	BMO	31.17	2.95	11.58	0.984	0.16	—
	CT	30.91	29.22	4.39	0.995	0.09	0.978

cient  $R$  of the overall correlation, the standard deviation  $\sigma$ , and the correlation coefficient  $r$  of the simple correlation of the solvent-induced shifts with only the cross function. Comparison of the correlation characteristics as well as comparison of the regression coefficients  $A$  with the transition wavenumbers measured in gas phase indicate that the cross term equation fits best the experimental data, and the correlation with only the cross term is better, too, in the case of one half of the systems investigated. The correlation coefficients of the correlations using the cross term equation are above 0.99 except for 4-nitro-N,N-diethylaniline ( $R = 0.988$ ).

With 4-nitroanisole (*III*), 4-nitro-N,N-diethylaniline (*V*), and 4-nitroso-N,N-dimethylaniline (*VI*) we carried out a comparison of the efficiency of the Bayliss–McRae–Ooshika method with the cross term method using the solvent set selected by Kamlet and Taft (SSS)<sup>7</sup>. The corresponding regression parameters and correlation characteristics are given in Table IV. Comparison of the correlation characteristics indicates that for SSS the two equations exhibit comparable efficiency. With the cross term equation the application of only selected solvents resulted practically in no change of the regression coefficients.

The cross term method also exhibits the best agreement between the transition wavenumber value of all the indicators found in the gas phase and the absolute term  $A$  of the correlation equations. The two remaining methods give a systematically higher value of the absolute term, as it is the case with application of the Bayliss–McRae–Ooshika method to the interpretation of the  $\pi^*$  parameters<sup>7</sup>.

The results of the regression analysis are interesting from the point of view of the empirical polarity scales derived from the solvatochromism of several indicators. Among them particularly interesting is the  $\pi^*$  scale by Kamlet and Taft which represents — without doubt — the most sophisticated and best applicable empirical scale

TABLE IV

Regression analysis of experimental data obtained for SSS carried out by means of the Bayliss–McRae–Ooshika (BMO) and the cross term (CT) methods

System (number of solvents)	Equation type	Parameter				
		$A$	$-B$	$-C$	$R$	$\sigma$
<i>III</i> (17)	BMO	37.10	3.31	14.24	0.992	0.19
	CT	36.86	36.75	6.08	0.995	0.15
<i>V</i> (16)	BMO	30.41	4.00	15.02	0.997	0.11
	CT	30.29	46.09	5.11	0.995	0.16
<i>VI</i> (15)	BMO	27.69	2.71	11.40	0.993	0.14
	CT	27.52	30.86	4.57	0.991	0.16

at present. All the three methods used by us for evaluation of solvent effects on electronic spectra of the indicators investigated indicate that the medium-induced changes in position of absorption maxima depend on two dielectrical characteristics – refractive index and relative permittivity or their functions, the contribution of these two functions to the overall effect being different for the individual indicators. Now there appears the question whether or not application of several indicators is suitable for adjusting a single polarity scale. The different contributions of the two functions to the overall medium effect obviously represent a reason of disproportions in the  $\pi^*$  parameter values determined by means of various indicators in the gas phase and in SSS<sup>14</sup> ( $-0.9$  to  $-1.2$ ).

The ratio of the regression coefficients  $B$  and  $C$  also obviously shows the reason why the mono-parameter equation only containing the cross term was so successful in interpretation of the  $\pi^*$  parameters<sup>11</sup> and also why it “missed” the  $\pi^*$  parameter of gas phase (although the assessment of this value was, out of the equations used for interpretation of the  $\pi^*$  parameters, one of the closest<sup>4,6,7,11,14-16</sup>). Within the SSS considered in the interpretation of the  $\pi^*$  parameters, the  $f(n^2)$  function varies from 0.180 to 0.220, a rough correlation being observed within this set between  $f(D, n^2)$  and  $f(n^2)$ . The  $f(n^2)$  function of the gas phase is equal to zero, hence from the point of view of this function the extrapolation concerns a region at a fivefold distance. Here the contribution of  $f(n^2)$  already becomes distinct, although it is five to ten times lower with the individual indicators than the contribution of the cross function  $f(D, n^2)$  to the overall effect of medium.

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