

Evaluation of medium effect on the absorption maxima of electronic spectra by Born's functions of relative permittivity and refractive index

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Regression analysis of the by medium induced changes in the absorption band position of ten model compounds showed that the product of the Born's functions of relative permittivity (ϵ_r) and refractive index (n) in the form $f(\epsilon_r, n^2) = (\epsilon_r - 1)/\epsilon_r \cdot (n^2 - 1)/n^2$ is more efficient for the evaluation of medium effect than recommended equations containing either Onsager's or Mossotti's functions of relative permittivity and refractive index. An excellent correlation ($R = 0.984$) was found between Kamlet—Taft's π^* polarity/polarizability parameters and the $f(\epsilon_r, n^2)$ function with the set of 54 aprotic aliphatic solvents.

Регресси́нный анализ изменений индуцированных средой в положении полосы поглощения десяти модельных соединений показал, что произведение функций Борна относительной диэлектрической проницаемости (ϵ_r) и показателя преломления (n) в форме $f(\epsilon_r, n^2) = (\epsilon_r - 1)/\epsilon_r \cdot (n^2 - 1)/n^2$ является более эффективным для оценки влияния среды, чем рекомендованные уравнения содержащие функции Онсагера или Моссотти относительной диэлектрической проницаемости и показателя преломления. Была найдена замечательная корреляция ($R = 0.984$) между параметрами полярность/поляризуемость π^* Камлета и Тафта и функцией $f(\epsilon_r, n^2)$ для комплекса 54 апротонных алифатических растворителей.

In 1920 *Born* [1] calculated the difference in work necessary for charging a conductive ball in a dielectricum and in air to be proportional to the function of relative permittivity (ϵ_r) of the dielectricum in the form $(\epsilon_r - 1)/\epsilon_r$. The function is still recommended [2] for the evaluation of medium effect on the properties of ions. For an evaluation of the medium effect on the properties of neutral molecules the methods based on the idea of the reaction field originally introduced by *Onsager* [3] are recommended. According to the concept the energy of a molecule in a solution is considered to be changed due to interactions between the solute and polarized solvent molecules of the solvation shells.

Depending on the starting model equations of various complexity have thus been obtained, the only characteristics of the medium being its relative permittivity and refractive index (n). As the electronic excitation of molecules connected with a considerable intramolecular charge transfer resembles the Born's conductor it seems to be interesting to extend the original Born's idea to a case of alternate charging of the conductor in a dielectricum with a frequency of 10^{15} Hz.

The aim of this paper was to perform an evaluation of medium effect on the position of absorption bands of electronic spectra of ten neutral dipolar compounds the spectra of which have been measured in a broad medium "polarity" range including vapour state by the product of Born's functions of relative permittivity and refractive index and by the conventional two-term equations of Onsager's and Mossotti's functions of relative permittivity and refractive index.

Results and discussion

Published wavenumbers of absorption maxima [4—6] of 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*), 3-nitroaniline (*IX*), and 3-nitrophenol (*X*) obtained in a great number of aprotic aliphatic solvents and vapour state were used for testing the equations considered.

The following correlation equations were tested:

Equation of Onsager's functions:

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

Equation of Mossotti's functions:

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

Equation of the product of Born's functions:

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

In the two-parameter equations of the Onsager's and Mossotti's functions the first term evaluates the contribution of the dipole—dipole interactions while the second the contribution of dipole—induced dipole interactions and of interactions related to dispersion forces to the medium effect observed. Besides the

given forms both the functions have been used in some modified ones [7—11]. In contradistinction to these methods, the equation of the product of the Born's functions does not consider the medium effect on electronic spectra as a result of the sum of all the solute—solvent interactions but treats the medium effect from the point of view of the work done during solvent polarization during the excitation process. The original Born's calculation [1] is extended to the case of alternate conductor charging with the frequency about 10^{15} Hz — the frequency being too high to be followed by orientational polarization of dielectric molecules. Only electronic deformational polarization of dielectric molecules is accomplished in this short time and therefore the work done by the molecules is proportional to the Born's function of refractive index $(n^2 - 1)/n^2 = f(n^2)_B$ only. Similarly the electronic excitation of a molecule connected with intramolecular charge transfer is a rapid process accomplished in 10^{-15} s. Immediately it is followed by the electronic deformational polarization of solvation shell molecules only. Their orientational polarization proceeds after 10^{-11} s so that it is without any effect on the energetical demand (and thus on the absorbed radiation quantum) of the excitation. As compared with the excitation of the molecule in the vapour state the excitation energy is lower, the decrease being proportional to the mentioned Born's function of refractive index $f(n^2)_B$. Magnitude of the decrease depends on the distance between the solute and solvation solvent molecules. The shorter is the distance the more intense is the deformational polarization and the deeper is the medium effect. As the first approximation the distance may be considered as depending on the total polarization of solvent molecules of solvation shells and thus being proportional to the Born's function of relative permittivity $f(\epsilon_r)_B$. The effect of the $f(n^2)_B$ is thus modified by the $f(\epsilon_r)_B$ term so that the final dependence of the spectral band wavenumber on the product of both the functions in the form of eqn (3) may be expected.

The efficiency of the modified Born's function and the equations of the Onsager's (eqn (1)) and Mossotti's (eqn (2)) functions for the evaluation of medium effect on electronic spectra (longwave maxima) of ten compounds is compared in Table 1. Both the correlation characteristics, *viz.* correlation coefficient (R) and standard deviation (σ) show that the simplest, only one-parameter, equation of Born's product term is more efficient than the two-parameter equations of the Mossotti's and Onsager's functions. The characteristics of the solvation spheres arrangement $f(\epsilon_r)_B$ may be expanded for $f(n^2)_B$ term characterizing polarization of solvation shell molecules due to rapid movements in solute molecule so that eqn (3) gets the form $\tilde{\nu} = A + B \cdot f(\epsilon_r)_B \cdot f(n^2)_B + C \cdot f^2(n^2)_B$, being, of course, more efficient than the original eqn (3).

When solvent effect of only nonpolar solvents ($\epsilon_r = n^2$) is considered eqns (1) and (2) are transformed to the dependence of the wavenumbers on the Onsager's

Table 1

Comparison of the results of the regression analysis of experimental data by the equation of Onsager's functions (OE), Mossotti's functions (ME), and by the modified Born's equation

Compound (Number of solvents)	Equation	$10^{-3} \cdot A$ cm ⁻¹	$10^{-3} \cdot B$ cm ⁻¹	$10^{-3} \cdot C$ cm ⁻¹	<i>R</i>	$10^{-3} \cdot \sigma$ cm ⁻¹
I (25)	OE	28.88	6.35	8.28	0.979	0.24
	ME	28.64	2.90	7.65	0.991	0.16
	Born	28.28	8.52	—	0.996	0.10
II (18)	OE	27.67	5.31	4.70	0.963	0.21
	ME	27.56	2.51	5.10	0.983	0.14
	Born	27.35	6.59	—	0.989	0.11
III (22)	OE	37.30	7.56	8.23	0.986	0.24
	ME	37.14	2.88	9.58	0.988	0.22
	Born	36.69	9.58	—	0.993	0.16
IV (18)	OE	35.16	11.60	8.86	0.977	0.37
	ME	34.90	5.32	9.98	0.990	0.24
	Born	34.45	13.19	—	0.994	0.17
V (21)	OE	30.61	9.00	7.78	0.983	0.28
	ME	30.48	3.65	9.78	0.983	0.28
	Born	30.29	11.36	—	0.990	0.20
VI (22)	OE	28.10	5.28	9.31	0.973	0.26
	ME	27.86	2.46	8.02	0.990	0.16
	Born	27.39	7.75	—	0.984	0.19
VII (10)	OE	37.33	8.30	4.25	0.988	0.18
	ME	37.45	3.67	6.23	0.990	0.22
	Born	37.27	9.22	—	0.997	0.11
VIII (19)	OE	28.72	5.54	5.89	0.967	0.24
	ME	28.52	2.53	5.71	0.988	0.15
	Born	28.19	6.66	—	0.992	0.11
IX (17)	OE	31.19	6.41	5.20	0.983	0.18
	ME	31.07	2.87	6.02	0.992	0.12
	Born	30.77	7.44	—	0.993	0.11
X (14)	OE	33.76	4.66	4.62	0.994	0.09
	ME	33.74	2.63	4.73	0.996	0.06
	Born	33.62	6.80	—	0.996	0.06

or Mossotti's functions of refractive index only, while the Born's product function is not changed. We carried out a comparison of the efficiency of these functions for the evaluation of medium effect of nonpolar solvents only (including also vapour state) on the electronic spectra of all the systems studied. The obtained results are given in Table 2. Calculated correlation characteristics point to the modified Born's function as the most efficient again.

Table 2

Comparison of the efficiency of the Born's product function, Onsager's function, and Mossotti's function of refractive index for the evaluation of the solvent effect of nonpolar solvents on the absorption maxima of the studied compounds

Compound (Number of solvents)	Product of Born's functions		Onsager's function		Mossotti's function	
	<i>R</i>	$10^{-3} \cdot \sigma/\text{cm}^{-1}$	<i>R</i>	$10^{-3} \cdot \sigma/\text{cm}^{-1}$	<i>R</i>	$10^{-3} \cdot \sigma/\text{cm}^{-1}$
<i>I</i> (8)	0.999	0.06	0.976	0.23	0.992	0.14
<i>II</i> (12)	0.995	0.07	0.966	0.16	0.984	0.11
<i>III</i> (4)	0.998	0.10	0.994	0.21	0.995	0.18
<i>IV</i> (11)	0.996	0.12	0.973	0.31	0.990	0.19
<i>V</i> (4)	0.998	0.12	0.988	0.30	0.992	0.25
<i>VI</i> (7)	0.998	0.07	0.986	0.19	0.996	0.10
<i>VII</i> (6)	0.995	0.11	0.983	0.21	0.988	0.17
<i>VIII</i> (11)	0.996	0.06	0.979	0.14	0.991	0.09
<i>IX</i> (10)	0.992	0.09	0.976	0.15	0.994	0.08
<i>X</i> (13)	0.997	0.05	0.989	0.10	0.993	0.07

Kamlet and *Taft* [12] used the solvatochromic behaviour of some compounds to make up a very popular polarity/polarizability solvent scale π^* . The scale has been a subject of various attempts of interpretation [5, 12—21]. We carried out a correlation of the π^* solvent characteristics with the product term of the Born's functions with 54 aliphatic, aprotic solvents and the resulting equation had the form

$$\pi^* = -0.94 + 3.66 \cdot f(\epsilon_r)_B \cdot f(n^2)_B \quad (4)$$

$$R = 0.984, \quad \sigma = 0.07$$

As for correlation characteristics and the estimation of the π^* of vapour state (experimentally the values between -0.90 and -1.12 have been determined) the present interpretation belongs to the most efficient.

The mutual correlation between the Born's product function and a sum of the Onsager's functions of relative permittivity and refractive index seems to be very interesting. For the set of by chance selected 60 solvents in the polarity range from *n*-pentane to dimethyl sulfoxide and diiodomethane the correlation has the form

$$f(\epsilon_r)_B \cdot f(n^2)_B = -0.243 + 0.838f(\epsilon_r)_0 + 1.65f(n^2)_0 \quad (5)$$

$$R = 0.997, \quad \sigma = 0.007$$

The correlation characteristics show that a close relation exists between the product of the Born's functions and the sum of both the Onsager's functions so

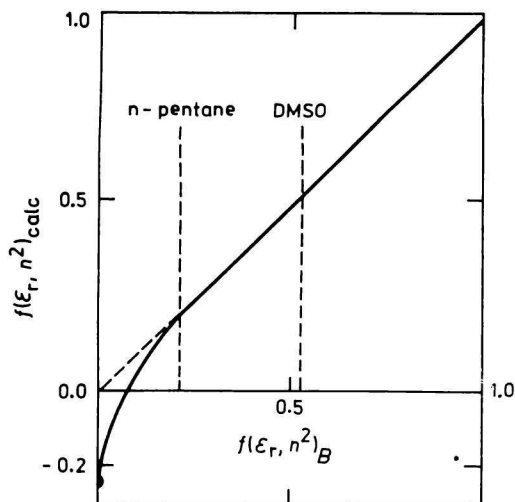


Fig. 1. Relation between the product of Born's functions of relative permittivity and refractive index $f(\epsilon_r, n^2)_B$ and the function calculated according to eqn (5) $f(\epsilon_r, n^2)_{\text{calc}}$.

that applicability of the both in the convenient "polarity" range should be nearly the same. In contradistinction to the expectation the intercept is different from zero, being -0.243 . The dependence is given in Fig. 1. From the graph it is apparent that over the range of common solvents (n-pentane—dimethyl sulfoxide) a linear dependence exists (by the way the linear dependence is obeyed by amphiprotic solvents as water, alcohols and formamide) but in the range between pentane and vapour state the linear dependence progressively deviates to -0.243 . The shape of this dependence clarifies the observed better applicability of the Born's product function over the Onsager one in the cases when data on electronic spectra obtained in perfluorinated hydrocarbons or even in vapour state are taken into account.

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