DIPOLE MOMENTS IN EXCITED STATE. SOLVATOCHROMIC EQUATIONS BASED ON DIFFERENT LOCAL-FIELD MODELS

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Two recent dielectric models, *viz.* the inverse exponential model of Block and Walker (BW) and the mean spherical model of Wertheim (W), were applied to the conceptually simple solvatochromic theory in the attempt to appreciate their ability to predict excited state dipole moments (μ_e) on the basis of the solvent dependence of electronic absorption spectra. Validity of the suggested equations was tested by standard methods of statistical analysis, as well as by comparison of the predicted μ_e values with those obtained independently from electrooptical measurements. All variants, including the original Onsager (O) formulation appear to be acceptable, the correlation coefficient varying from 0·920 to 0·982. However, they predict different μ_e values the order of magnitude being (for a given solute) invariably $(\mu_e)^{BW} > (\mu_e)^{O} > (\mu_e)^{W}$. In view of the large uncertainties in the cavity radius *a*, no unambiguous conclusions can be drawn on the preference of the respective models. Provided that the mean polarizability α is approximated by $\alpha = a^3/2$, the most satisfactory results (mean relative error in μ_e of about $\pm 6\%$, $R = 0{\cdot}930-0{\cdot}960$) are obtained by using the reaction field model of Block and Walker.

The solvent-induced shifts of electronic absorption bands (solvatochromism) has been used extensively as a source of information about the change of electron density with excitation and resulting electron distribution of electronically excited molecules[1-10]. The most readily available quantity is the vector difference in permanent dipole moments, $\Delta\boldsymbol{\mu}(\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_e - \boldsymbol{\mu}_g)$, between the excited and ground state subscribed *e* and *g*, respectively. Several reviews on the subject have appeared[6-10] and new studies are still continuing[11-16], despite the known limitations[17] of the method for the quantitative evaluation of $\boldsymbol{\mu}_e$.

In deriving the pertinent solvatochromic equations, perturbation theory results are related to solute and solvent macroscopic parameters (*e.g.* μ_e, μ_g, α and ε, n) by applying the reaction field model[18,19] and identifying the terms with classical electrostatic interactions, *e.g.* dipole–dipole and dipole-induced dipole.

According to the reaction field formalism[18,19] the interaction energy of the solute dipole with the dielectric is given as $\Delta E_i = E_i - E_i^0 = -1/2\boldsymbol{\mu}\boldsymbol{R}$, where E_i is the *i*-th state energy in the solvent, E_i^0 is the corresponding energy *in vacuo* and $\boldsymbol{R}$ is the reaction field, *i.e.* the field which arises by polarization of the surrounding and acts

back on the dipole. Since there are two mechanisms for production of reaction fields, orientational and induced polarizations, the total reaction field $\boldsymbol{R}$ can be partitioned as a sum of these two contributions, *i.e.* $\boldsymbol{R} = \boldsymbol{R}_{or} + \boldsymbol{R}_{in}$, where

$$\boldsymbol{R} = \boldsymbol{f}\boldsymbol{\mu}(1 - \alpha\boldsymbol{f})^{-1} \tag{1a}$$

$$\boldsymbol{R}_{in} = \boldsymbol{f}'\boldsymbol{\mu}(1 - \alpha\boldsymbol{f}')^{-1} \tag{1b}$$

$$\boldsymbol{R}_{or} = (\boldsymbol{f} - \boldsymbol{f}')\,\boldsymbol{\mu}[(1 - \alpha\boldsymbol{f})\,(1 - \alpha\boldsymbol{f}')]^{-1} \tag{1c}$$

Here, α represents an average polarizability, $\boldsymbol{f}$ and $\boldsymbol{f}'$ are generally the reaction field tensors. Usually the solvent is approximated by a homogeneous and isotropic dielectric where the solute molecules are localized in cavities with a definite shape. In the most simple case the shape of the cavity is assumed to be spherical; then the tensors $\boldsymbol{f}$ and $\boldsymbol{f}'$ are reduced to scalars f and f'. If furthermore the dipole of the solute is approximated by a point dipole localized at the center of the sphere, then

$$\boldsymbol{f} = f\,.\,\boldsymbol{I} = 2a^{-3}(4\pi\varepsilon_0)^{-1}(\varepsilon_B - 1)/(2\varepsilon_B + 1)\,.\,\boldsymbol{I} \tag{2}$$

and

$$\boldsymbol{f}' = f'\,.\,\boldsymbol{I} = 2a^{-3}(4\pi\varepsilon_0)^{-1}\,(n^2 - 1)/(2n^2 + 1)\,.\,\boldsymbol{I} \tag{3}$$

with a being the radius of the sphere, ε_0 the permittivity of the vacuum, ε_B the bulk relative dielectric constant and n the refractive index.

Assuming that the solvent reorientation is slow compared to the absorption process in accordance with the Franck–Condon principle, the shift in transition energy upon solvation is

$$\Delta E = \Delta E_e - \Delta E_g = hc\,\Delta\nu = -1/2(\mu_e R_e^{FC} - \mu_g R_g)\,. \tag{4}$$

Numerous approximations underlying the original theoretical treatment together with further simplifications in deriving final solvatochromic equations were already reviewed[6,9]. Despite the differences in approximations involved, all current solvatochromic theories lead finally to similar expressions. If we (*1*) restrict ourselves to molecules having symmetry axis, (*2*) ignore any changes in polarizability on excitation ($\alpha = \alpha_g = \alpha_e$) and introduce the notation

$$B_1 = \mu_g(\mu_e - \mu_g) \qquad B_2 = 0{\cdot}5(\mu_e^2 - \mu_g^2)$$

$$B_2' = 0{\cdot}5(\mu_e - \mu_g)^2 \qquad B_2'' = \mu_e(\mu_e - \mu_g)\,,$$

the resulting equations may be summarized as shown in Table I.

In a recent paper[11] we have tested the validity of these (and related) equations for the determination of excited state dipole moments using expressions for f and f' given by Eq. (2) and (3). It was found that (*i*) each of the equations may be rewritten as a linear sum of terms in product function form

$$\Delta E_{ik} = \sum_{j=1}^{r} B_{ij} \, . \, F_{jk} + C \, , \tag{5}$$

where B_{ij} is a solute factor depending exclusively on the solute i properties and F_{jk} is a solvent factor characterized by the solvent k macroscopic properties, and (*ii*) Eqs (5*a*) and (5*b*) led generally to better agreement with electrooptical experiments than the other equations.

So far, the theory of solvent shifts has been treated almost exclusively within the Onsager reaction field model. Although constantly (and justly) criticized for its oversimplification of reality and other shortcomings, the Onsager model provides an invaluable starting point in the evolution of more sophisticated approaches. There are two obvious flaws in the Onsager model. In the vicinity of the polar solute molecule, the solvent may be oriented by the electric field of the dipole, and its dielectric constant there will be much lower than the bulk value used in Eq. (2). Furthermore, for a given solute dipole, the reaction field of Onsager reaches[20] 85% of its maximum possible value at $\varepsilon_B \approx 12$, but it was experimentally found that the solvent effect increased appreciably for solvents with $\varepsilon_B > 12$. Both these flaws are due to the representation of the field factor f by Eq. (2) which therefore needs improvement, or perhaps even replacement. On the other hand, the electronic polarization should not be subjected to saturation effects to that extent as are orientational processes.

TABLE I

Basic equations describing the solvent effect on absorption spectra

Eq.[a]	ΔE_{e-g}	Ref.
5*a*	$B_1[f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] + B_2 f'$	1
5*b*	$B_1(1-\alpha f')^{-1}[f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] + B_2 f'(2-\alpha f)(1-\alpha f')^{-2}$	2, 3
5*c*	$B_1 f(1-\alpha f)^{-1} + B_2' f'(1-\alpha f')^{-1}$	6
5*d*	$B_1 f + B_2' f'$	4
5*e*	$B_1 f(1-\alpha f)^{-1} + B_2'' f'(1-\alpha f')^{-1}$	5[b]

[a] Both the dispersion and temperature dependent terms are ignored in all equations; [b] original work uses an equivalent equation $\Delta E_{e-g} = 0{\cdot}5\mu_g^2 f(1-\alpha f)^{-1} - 0{\cdot}5\mu_e^2 f'(1-\alpha f')^{-1} - 0{\cdot}5\mu_e\mu_g(f-f')(1-\alpha f)^{-1}(1-\alpha f')^{-1}$.

Therefore, it could be well described by the reaction field factor f' as defined by Eq. (3).

Various local-field models have been proposed which, removing the Onsager discontinuity, include the concept of local order at the boundary achieving the appropriate bulk dielectric constant at large distances. Examples of such reaction field models are those of Block and Walker[21], Wertheim[22] and Fulton[23]. To include continuous permittivity variation across the cavity boundary, Block and Walker[21] attempted an analytical solution of the modified Laplace equation for the radial potential by assuming a spatial dependence of the permittivity in the form $\varepsilon(r) = \varepsilon_B \exp\left[-a(\ln \varepsilon_B)/r\right]$ for $r > a$. At $0 \leqq r \leqq a$, $\varepsilon(r) = 1$. Accordingly, the corresponding reaction field, R^{BW}, is established as

$$R^{BW} = (\mu a^{-3})(4\pi\varepsilon_0)^{-1}\left[3\varepsilon_B \ln \varepsilon_B/(\varepsilon_B \ln \varepsilon_B - \varepsilon_B + 1) - (6/\ln \varepsilon_B + 2)\right] = f^{BW} \cdot \mu = (2\mu a^{-3})(4\pi\varepsilon_0)^{-1} F(\varepsilon)^{BW} . \quad (6)$$

For comparison, the mean spherical model of Wertheim[22], where analytic potentials representing fluids are modelled as composed of hard spheres may also be cast in terms of classical fields. It has been shown[22,24] that the reaction field appropriate for polar liquid is proportional to the intrinsic variable ξ (molar volume, pair distribution, and correlation function dependent), which is in turn a function of the bulk dielectric constant, $\varepsilon_B = (1 + 4\xi)^2 (1 + \xi)^4 (1 - 2\xi)^{-6}$. The corresponding reaction, field, R^W, may be written as

$$R^W = (\mu a^{-3})(4\pi\varepsilon_0)^{-1} 16\xi = f^W \cdot \mu = (2\mu a^{-3})(4\pi\varepsilon_0)^{-1} F(\varepsilon)^W . \quad (7)$$

In this paper we note that, in addition to the Onsager field, any local field can be used as the driving field in deriving the solvatochromic equations. Among the fields mentioned above, however, the Fulton's one is exceptional since it takes account of the microscopic structure of the medium by modelling the solution as a rigid cubic lattice. Here, we restrict our analysis to a comparison of the results based on the Onsager field with those derived using Block–Walker and Wertheim local-field models, which we believe to be more realistic than other theories. To our knowledge, no such attempt has been made in the previous works concerning excitated state dipole moment determination.

The aim of this communication is (1) to modify the practically used solvent-shift equations by involving Block–Walker and Wertheim reaction field models, and (2) to check the validity of the modified equations for the determination of correct solvent shifts and excited state dipole moments, by comparing predicted quantities with corresponding values obtained experimentally from independent measurements.

As model compounds we have chosen nitrobenzene (*I*), 4-aminonitrobenzene (*II*), 4-dimethylaminonitrobenzene (*III*) and N-methylacridone (*IV*). The selection of these compounds was dictated (*1*) by the availability of sufficient number of the solvent-dependent spectral data to allow serious statistical analyses, (*2*) by the presence of symmetry axis (or at least by the expected collinearity $\mu_e \parallel \mu_g$), and (*3*) by the knowledge of the μ_e values from the more reliable electrooptical measurements.

EXPERIMENTAL

The wavenumbers ν_a for compounds *I*—*IV* in various solvents together with several molecular properties of the compounds needed for the analysis were taken from original papers (Table II). Values of dielectric constant (ε_B) and refractive indices (n) at 25°C, taken from the recomended sources[37] served as a uniform basis for the determination of working solvent functions $F(\varepsilon)$ and $F(n)$. Numerical values of these functions were calculated on Hewlett-Packard 9830A calculator.

The linear least squares multiple regression program (Hewlett-Packard Standard statistic Pac No 2) was used to fit Eqs (*5a*)—(*5d*) to the data yielding the best fit parameters B_1, B_2 and ν_0. All points exhibiting deviation 2—3 times greater than the standard deviation were excluded from the regression. The omitted points correspond mostly to solvents which frequently exhibit anomalous behaviour (dioxan, hydroxylic and polychlorinated solvents). The quality of the fit is illustrated in Fig. 1 by plotting observed *vs* calculated wavenumber shifts (Eq. (*5d*), Block-Walker model) for 4-dimethylaminonitrobenzene (*III*).

RESULTS AND DISCUSSION

The expressions for the frequency shift (Eqs (*5a*)—(*5d*), Table I) form the central point of our analysis.* They are presented in a form permiting direct comparison of the three local-field models investigated, *viz.* the inverse exponental model of Block and Walker, the mean spherical model of Wertheim and the classical model of Onsager. Using the explicit expressions for reaction field factors f corresponding to these models (Table III), the only parameter to be specified is the mean polarizability α. There is uncertainty, however, as to the proper polarizability to employ in the calculations. Of the four equations mentioned above the Eq. (*5d*) is exceptional in that it, since based on an unpolarizable dipole, automatically assumes $\alpha = 0$. Exact solution of the Eqs (*5a*)—(*5c*) may be found if α can be expressed in terms of the radius cavity a. Hence, $\alpha = a^3/2$ has been employed throughout this work. As an advantageous consequence, the general form of Eq. (*5*) is retained, the only difference among the Eq. (*5d*) and Eqs (*5a*)—(*5c*) being the form of the resulting solvent function $F(\varepsilon)$.

* As no substantial difference exists between Eqs (*5c*) and (*5e*), only the former will be considered in this work.

TABLE II

Physical constants of model compounds

Compound	$\mu_g \cdot 10^{30}$ [a] Cm	$\mu_e \cdot 10^{30}$ [b] Cm	$a \cdot 10^8$ cm	ν_{gas} [c] cm^{-1}	Ref.[d]
I	13·09	29·97	3·20[c]	41 667	27
II	20·94	51·61	3·45[c]	34 210	28
III	22·81	49·95	3·68	—	29, 30
IV	17·98	24·31	3·60[e]	—	31

[a] Ref.[25]; [b] electrooptical values, ref.[26]; [c] ref.[12]; [d] the references give wavenumbers; [e] ref.[4].

TABLE III

Comparison of different local-field models

Model	ε_{eff}	$fa^3(8\pi\varepsilon_0)^{-1}$
Onsager (O)	ε_B	$\varepsilon_B - 1/2\varepsilon_B + 1$
Block–Walker (BW)	$\varepsilon_B \exp[-a(\ln \varepsilon_B)/r]$	$3\varepsilon_B \ln \varepsilon_B/(2\varepsilon_B \ln \varepsilon_B - 2\varepsilon_B + 2) - 3/\ln \varepsilon_B - 1$
Wertheim (W)	[a]	8ξ

[a] In the case of Wertheim model, equation $\varepsilon_B = (1 + 4\xi)^2 (1 + \xi)^4 (1 - 2\xi)^{-6}$ can be inverted numerically to determine the parameter ξ as the function of ε_B; over the usual range of interest, $1 < \varepsilon_B < 100$, an approximate solution is given by $\xi = (1/24) \ln \varepsilon_B$.

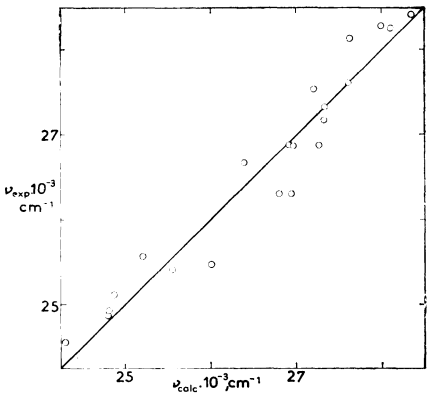

FIG. 1

Graphical representation (left side *vs.* right side) of the equation (*5d*) in Block–Walker version for 4-dimethylaminonitrobenzene(*III*)

Strictly speaking, the polarizability of the sphere is related to the refractive index and radius a in the ideal case by $\alpha = a^3(n^2 - 1)/(n^2 + 2) = Ka^3$. If, for example, a^3 is determined from kinetic theory, the α/a^3 increases from 0·22 for helium to 0·74 for xenon, giving a mean value of $K = 1/2$ which is used by many authors. Consequently, the functional form of $F(\varepsilon)^0$ changes from $(\varepsilon_B - 1)/(2\varepsilon_B + 1)$ corresponding to $\alpha = 0$, to $(\varepsilon_B - 1)/(\varepsilon_B + 2)$. On the other hand, since n^2 for a wide range of aromatic molecules is[16] $2{\cdot}56 \pm 0{\cdot}32$, the most reasonable approximation should be $\alpha = a^3/3$. This value would change the solvent function $F(\varepsilon)^0$ to $3(\varepsilon_B - 1)/(4\varepsilon_B + 5)$. Taking into account the large uncertainties connected with the cavity radius estimation (see below) together with the fact that an errror of about 14·5% in a (resulting from the assumed equality $a_1 = (2/3)^{1/3} a_2$) can completely compensate the difference between $\alpha = a^3/2$ and $\alpha = a^3/3$, we consider the frequently used approximation $\alpha = a^3/2$ to be satisfactory. Anyhow, of the two cases, $\alpha = 0$ and $\alpha = a^3/2$, the former represents a more crude approximation.

Restricting first ourselves to the case of nonpolarizable dipole ($\alpha = 0$), the solvent functions $F(\varepsilon)$ corresponding to particular models may be compared as shown in Fig. 2, where for a given solute, functions $F(\varepsilon)^{BW}$ and $F(\varepsilon)^{W}$ are plotted as a function of $F(\varepsilon)^0$. Upon identifying the Fulton's parameters d^2 and v as proposed by Deutch[32], the Fulton solvent function $F(\varepsilon)^F$ is also presented for illustration. Interestingly, the $F(\varepsilon)^{BW}$ and $F(\varepsilon)^F$ show a similar type of behavior. It follows from the inspection of the plot that both the Block–Walker and Wertheim model predict a large difference from the Onsager one, especially for higher values of ε_B. Over the range $2 < \varepsilon_B < 50$, which covers most of the solvents commonly used, $F(\varepsilon)^0$ varies by *c.*0·3 while $F(\varepsilon)^{BW}$ and $F(\varepsilon)^{W}$ vary by *c.* 0·19 and 1·05, respectively.

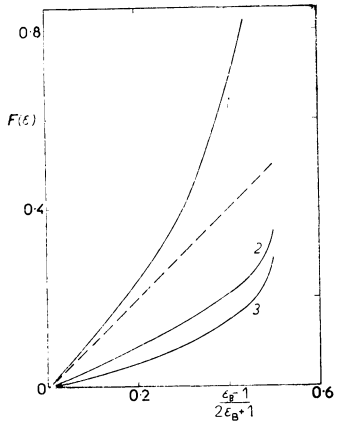

FIG. 2

Solvent parameters $F(\varepsilon)$ according to Block–Walker (BW), Wertheim (W) and Fulton (F) models ($\alpha = 0$), as a function of $(\varepsilon_B - 1)/(2\varepsilon_B + 1)$. Straight line of unit slope corresponds to the Onsager model; *1* $F(\varepsilon)^W$, *2* $F(\varepsilon)^F$, *3* $F(\varepsilon)^{BW}$

Writing Eq. (*5d*) for each of the models examined in the form

$$\Delta E = -2\mu_g a^{-3}(\Delta\mu)^{O}\,\Delta F(\varepsilon)^{O} - (\mu_e^2 - \mu_g^2)\,a^{-3}\,\Delta F(n)\,, \qquad (5d, \mathrm{O})$$

$$\Delta E = -2\mu_g a^{-3}(\Delta\mu)^{BW}\,\Delta F(\varepsilon)^{BW} - (\mu_e^2 - \mu_g^2)\,a^{-3}\,\Delta F(n)\,, \qquad (5d, \mathrm{BW})$$

$$\Delta E = -2\mu_g a^{-3}(\Delta\mu)^{W}\,\Delta F(\varepsilon)^{W} - (\mu_e^2 - \mu_g^2)\,a^{-3}\,\Delta F(n)\,, \qquad (5d, \mathrm{W})$$

where $F(n) = (n^2 - 1)/(2n^2 + 1)$

and taking into account variances in $F(\varepsilon)$ described above, the immediately following implication is that for a given solute the predicted μ_e values would be approximately in the relation $(\Delta\mu)^{BW} \approx 1{\cdot}5(\Delta\mu)^{O}$ and $(\Delta\mu)^{W} \approx 0{\cdot}3(\Delta\mu)^{O}$.

Tables IV to VII summarize the results of statistical analyses of the data for compounds *I*–*IV*. Still accepting Eq. (*5d*) as a base for the discussion, we note that

TABLE IV

Statistics of Eq. (*5*) for nitrobenzene (*I*)[a]

Model	Eq.	R[b]	ν_0[c] cm^{-1}	B_1/B_2[d]	F_1[e]	F_2[e]	$\mu_e \cdot 10^{30}$ Cm
O	*5a*	0·972	41 656	− 2 060	268·3	9·5	18·7
				−10 807			
	5b	0·971	41 005	− 1 670	264·6	8·4	17·7
				− 5 357			
	5c	0·972	41 263	− 2 060	273·8	5·1	18·7
				− 5 014			
	5d	0·982	41 849	− 4 864	430·3	6·3	26·5
				− 6 809			
BW	*5a*	0·953	42 174	− 6 650	141·8	15·6	31·4
				−19 999			
	5b	0·953	41 254	− 5 400	141·8	16·9	28·0
				−10 997			
	5c	0·952	41 427	− 6 637	152·2	4·6	31·4
				− 6 360			
	5d	0·962	41 803	− 8 860	191·6	5·2	37·5
				− 9 249			
W	*5d*	0·950	41 817	− 1 593	142·7	4·5	17·5
				−10 007			

[a] Final number of solvents $n = 19$; [b] multiple correlation coefficient; [c] intercept; [d] coefficients of Eq. (*5*); [e] partial F-tests.

from the statistical point of view all reaction fields examined appear to be acceptable, the multiple correlation coefficient varying from 0·920 to 0·982 with most values greater than 0·940. Moreover, partial F-tests support in all cases the reliability of both terms in Eq. (*5d*) at the 99% confidence level. Hence, the dipole-induced dipole and/or dispersion interactions are generally operative and any single parameter correlation based exclusively on the $F(\varepsilon)$ function would be inadequate. Concerning excited state dipole moments, the respective reaction field models afford different results. Whereas (and somewhat surprisingly) all μ_e values based on the classical Onsager model are found to agree within $\sim \pm 10\%$ with the electrooptical data (Fig. 3*a*), the Block–Walker model tends to overestimate μ_e values and the opposite is true for the Wertheim model. It should be pointed out, however, that Wertheim takes $a = d$, the exact hard sphere diameter in deriving his equation. Bearing in mind that slopes B_1 relate $\Delta\mu a^{-3}$ and realizing that in the context of this paper the radius a could adopt a value less than d, our results based on the Wertheim model likely give the lower limits to the true values.

TABLE V

Statistics of Eq. (*5*) for 4-aminonitrobenzene (*II*)[a]

Model	Eq.	R[b]	ν_0[c] cm^{-1}	B_1/B_2[d]	F_1[e]	F_2[e]	$\mu_e \cdot 10^{30}$ Cm
O	*5a*	0·945	34 351	− 5 712	224·3	16·3	33·3
				−20 386			
	5b	0·941	32 731	− 4 539	213·6	11·7	30·7
				− 8 803			
	5c	0·944	33 463	− 5 704	232·7	5·3	33·3
				− 7 027			
	5d	0·935	34 213	−13 621	200·9	2·0	50·3
				− 4 450			
BW	*5a*	0·930	34 409	−15 091	152·5	34·4	53·5
				−36 759			
	5b	0·932	32 722	−15 091	153·0	38·9	47·0
				−20 094			
	5c	0·930	32 864	−15 085	180·5	5·5	53·5
				− 8 059			
	5d	0·941	33 782	−21 494	216·2	6·3	67·3
				−12 596			
W	*5d*	0·920	33 479	− 3 580	149·2	5·5	28·7
				−13 513			

[a] Final number of solvents $n = 32$; [b,c,d,e] see Notes[b,c,d,e], Table IV.

TABLE VI

Statistics of Eq. (5) for 4-dimethylaminonitrobenzene (*III*)[a]

Model	Eq.	R^b	$\nu_0{}^c$ cm^{-1}	$B_1/B_2{}^d$	$F_1{}^e$	$F_2{}^e$	$\mu_e \cdot 10^{30}$ Cm
O	*5a*	0·977	32 754	− 4 095 −19 664	312·0	69·7	32·7
	5b	0·976	32 067	− 3 257 −15 080	298·0	61·2	30·7
	5c	0·977	33 703	− 4 090 −24 305	326·7	42·2	32·7
	5d	0·977	34 914	− 9 745 −25 279	327·3	46·2	46·4
BW	*5a*	0·960	31 884	−12 009 −26 026	146·4	67·1	51·9
	5b	0·958	31 482	− 9 536 −21 663	134·3	68·9	45·9
	5c	0·960	32 754	−11 999 −21 914	190·2	20·2	51·9
	5d	0·968	33 144	−16 488 −22 554	237·7	26·5	62·8
W	*5d*	0·957	32 653	− 2 840 −21 685	175·9	18·4	29·7

[a] Final number of solvents $n = 21$; [b,c,d,e] see Notes[b,c,d,e], Table IV.

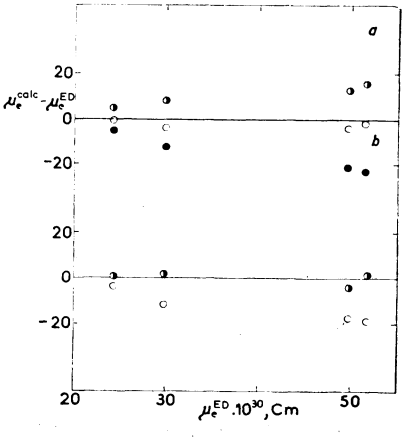

FIG. 3

Residual plots for the solvatochromic determination of μ_e; (*a*) $\alpha = 0$ (Eq. (*5d*)), (*b*) $\alpha = a^3/2$ (Eq. (*5a*)).

When the more realistic assumption $\alpha = a^3/2$ is used, the Wertheim solvent function $F(\varepsilon)^W = 8\xi(1 - 8\xi)^{-1}$ diverges as ξ approaches the value of 1/8 thus, for a wide range of solvents, not allowing full comparison with the other reaction field models. As regards the overall evaluation of the solvent-shift methods based on the Block–Walker and Onsager model we draw attention to the following: *1*) the differences among the Eqs (*5a*)–(*5c*), caused mainly by perturbing $F(n)$ function in the first term, are not very significant for both models. Contrary to the variation range of the dielectric constant term, $F(\varepsilon)[1 - F(\varepsilon)]^{-1}$, (0·7084 and 0·2514 units on going from n-hexane to dimethyl sulfoxide using $F(\varepsilon)^0$ and $F(\varepsilon)^{BW}$, respectively) the correcting term $(n^2 - 1)/(n^2 + 2)$ may be considered constant varying at most by 0·06 around a mean value of 0·26 in our systems. As a consequence, Eqs (*5a*) and (*5b*) may be regarded as unsubstantial modifications of the Eq. (*5c*), all predicting practically the same values of μ_e, maximum difference among them being about 8% for the Onsager model and about 12% for the Block–Walker model. Margina

TABLE VII

Statistics of Eq. (*5*) for N-methylacridone (*IV*)[a]

Model	Eq.	R^b	ν_0^c / cm^{-1}	$B_1/B_2{}^d$	$F_1{}^e$	$F_2{}^e$	$\mu_e \cdot 10^{30}$ / Cm
O	*5a*	0·955	27 008	− 881 −7 217	192·1	70·0	20·5
	5b	0·953	26 524	− 698 −3 409	186·0	59·0	19·9
	5c	0·955	26 704	− 882 −3 667	215·0	45·7	20·5
	5d	0·956	26 906	−2 118 −3 576	221·0	44·2	24·0
BW	*5a*	0·946	27 023	−2 517 −9 948	127·1	77·0	25·2
	5b	0·944	26 483	−1 997 −5 130	120·1	78·5	23·7
	5c	0·946	26 607	−2 523 −3 757	174·7	30·2	25·2
	5d	0·957	26 978	−3 638 −6 214	216·0	41·1	28·4
W	*5d*	0·932	26 720	− 600 −5 258	144·7	21·0	19·7

[a] Final number od solvents $n = 29$; [b,c,d,e] see Notes[b,c,d,e], Table IV.

change in correlation coefficient indicates that none of the Eqs (*5a*) to (*5c*) is demonstrably superior. *2*) Both models are roughly comparable as regards the quality of the linear fit. *3*) μ_e values obtained by using the Onsager model are invariably about 20–40% lower than those obtained by using the Block–Walker model and *4*) the Block–Walker model predicts μ_e values which agree very well (relative error ±6·4%) with electrooptical data (Fig. 3*b*).

Concerning ν_{gas} values a comparison between our results and those obtained experimentally is limited to nitrobenzene (*I*) and 4-aminonitrobenzene (*II*) for which experimental data are available (Table II). The agreement between the calculation and experiment is rather good in most cases, *e.g.* the differences for Eq. (*5a*) in the BW version being +507 and +322 cm^{-1}, respectively. Such a consistency, however, is rather surprising and should be regarded with caution. It has been stressed by many authors[6,9] that the shift given by Eq. (*5*) must be considered as superimposed on a general red shift which is present in all solution spectra and independent of the solute dipole. On account of this general red shift it is not advisable to use vapor phase measurement as a reference point.

The agreement of calculated and experimental data demonstrates impressively the general validity of the concept presented in this paper. At this point, however, we must comment on the accuracy of the results. The most glaring deficiency in the calculation arises in the treatment of cavity radius a. Since all the parameters f involve the third power of the radius, the value of a assumed has a very large effect on the μ_e values predicted. Unfortunately, the cavity radius is not a well defined parameter and there is considerable arbitrariness in its determination. Several procedures which have been proposed including (*i*) equivalent shell model[33], (*ii*) addition of van der Waals volume increments[4], (*iii*) densitometric and polarization measurements[13,27] and (*iv*) simple geometric consideration[15], afford different results. To illustrate this phenomena we have calculated μ_e values for nitrobenzene (*I*) using Eq. (*5*) and adopting different radii as preferred by various authors.

It may be seen from Table VIII that μ_e values based on the cavity radius $a = 3{\cdot}44 \,.\, 10^{-8}$ cm (densitometric) are, depending on the working equation, about 50–100% higher than those calculated from $a = 1{\cdot}63 \,.\, 10^{-8}$ cm (geometric consideration). This raises an interesting question, yet to be answered, for the general solvatochromic theory: What molecular radius should be used in the solvent-shift equations? We shall not attempt a general discussion of this problem here, but taking into account the experimental value of the average molecular polarizability for nitrobenzene[34] ($\alpha = 12{\cdot}92 \,.\, 10^{-24}$ cm^3) together with the fact that this quantity should be related to the cavity radius by the relation $\alpha = a^3/2$ or $\alpha = a^3/3$, we can expect for nitrobenzene a value for a between $2{\cdot}96 \,.\, 10^{-8}$ and $3{\cdot}38 \,.\, 10^{-8}$ cm. Thus, the method proposed by Prabhumirashi[15] yielding for nitrobenzene $a = 1{\cdot}63 \,.\, 10^{-8}$ cm seems to be unrealistic.

Let us finally briefly discuss, in the light of the present approach, the empirical two-parameter model which has been used by Sjöström and Wold[35] to obtain systematic information about the solvatochromic shift data on the basis of principal component analysis combined with a cross-validation technique. They showed that (*1*) two parameters Z_{1k} and Z_{2k} (Eq. (*8*)) for each

$$\nu_{ik} = \nu_{ik}^0 + \sum_{j=1}^{r} Y_{ij} Z_{jk} + \beta_{ik} \qquad (8)$$

solvent are needed to describe the systematic change in solvatochromic shifts, and (*2*) the Z_{2k} values are highly correlated with the polarizability of the solvent, *i.e.* with its refractive index. As Eq. (*8*) represents an equivalent of our Eq. (*5*), these findings provide some additional justification for using two parameters in Eq. (*5*), one of them being the $F(n)$ function. By analogy, the Z_{1k} parameters can be thought as an equivalent of our $F(\varepsilon)$ functions. Consonant with this expectation, Z_{1k} values for 21 commonly used solvents (hexane, heptane, cyclohexane, tetrachloromethane, 1,2-dichloroethane, chlorbenzene, ethyl acetate, diethyl ether, di-n-butyl ether, acetone, butan-2-one, cyclohexanone, tetrahydrofuran, triethylamine, pyridine, nitromethane, dimethyl sulfoxide, dimethylacetamide, dimethylformamide, acetonitrile and benzonitrile) are satisfactorily linear with the solvent functions $F(\varepsilon)$, as shown in Eqs (*9*)–(*11*).

$$Z_{1k} = 8{\cdot}20 - (20{\cdot}49 \pm 1{\cdot}40)F(\varepsilon)^0 \qquad (9)$$

$$R = 0{\cdot}595\,, \quad F = 215{\cdot}3$$

$$Z_{1k} = 5{\cdot}46 - (33{\cdot}94 \pm 2{\cdot}65)\,F(\varepsilon)^{BW} \qquad (10)$$

$$R = 0{\cdot}947\,, \quad F = 164{\cdot}4$$

TABLE VIII

μ_e Values for nitrobenzene as predicted by Eq. (*5*) using different cavity radii

$a \cdot 10^8$ cm	$\mu_e \cdot 10^{30}$ Cm	
	Eq. (*5a*, 0)	Eq. (*5d*, 0)
1·63[a]	13·9	14·9
3·20[b]	19·1	27·3
3·44[c]	20·6	30·8

[a] Ref.[15]; [b] ref.[12]; [c] ref.[27].

$$Z_{1k} = 4{\cdot}67 - (5{\cdot}70 \pm 0{\cdot}51)\, F(\varepsilon)^{W} \qquad (11)$$

$$R = 0{\cdot}931\,, \quad F = 122{\cdot}7$$

Similar equations (even with a slightly better correlation coefficient R) may be written for the "cation-solvating tendency" B, being the solvent parameter proposed very recently by Swain[36] on the basis of a different approach. For the select set of 21 solvents, however, the parameters Z_{1k} and B are interrelated by Eq. (*12*).

$$B = 0{\cdot}672 - 0{\cdot}147 Z_{1k} \qquad (12)$$

$$R = 0{\cdot}992\,, \quad F = 1\,179$$

Concerning the overall evaluation of the solvent-shift equations proposed in this paper, we can summarize that *1*) about 86–94% of variability in $\Delta\nu$ can be ascribed to $F(\varepsilon)$ and $F(n)$ parameters, irrespective of the reaction field model used; in addition, reliability of the solvent functions $F(\varepsilon)$ is supported by their statistically significant correlations with the more general parameters Z_{1k} and B; *2*) two variants give excited state dipole moments comparable with electrooptical measurements. The first of them is based on the Onsager model assuming $\alpha = 0$, the second is based on the Block–Walker model assuming $\alpha = a^3/2$. We can not choose unambiguously between them because of their nearly comparable statistics, but we prefer the Block–Walker variant since it is more rigorous both in the approximation of α and the realistic conception of the local permittivity at the boundary; *3*) optimum results (mean relative error $\pm 6{\cdot}4\%$) are obtained using equation

$$\Delta E = \frac{-2\mu_g\,\Delta\mu}{4\pi\varepsilon_0 a^3}\left[\frac{X + Y - 2\varepsilon_B - 1}{X - Y + \varepsilon_B + 2} - \frac{n^2 - 1}{n^2 + 2}\right] - \frac{(\mu_e^2 - \mu_g^2)}{4\pi\varepsilon_0 a^3}\,\frac{n^2 - 1}{2n^2 + 1}\,,$$

which represents the explicit form of Eq. (*5a*) in the Block–Walker version. In this equation $X = 0{\cdot}5\varepsilon_B \ln \varepsilon_B$ and $Y = 3(\varepsilon_B - 1)(\ln \varepsilon_B)^{-1}$; *4*) it is necessary to be extremely cautious when applying solvent shift theory to systems for which the molecular parameters are not very well-known.

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