J. Am. Chem. Soc. **1981**, *103*, 6036-6043

Classical Electrical Contributions to Solvent Polarity Scales[†]

S. Ehrenson

Contribution from the Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973. *Received February 23, 1981*

Abstract: Simple individual-molecule dipole reaction field models for solvation are delineated and compared with continuum models, particularly as regards correlation of various solvent polarity scales. Of central interest is the π^* scale for which only minor differences in correlational ability are observed between the model extremes as well as among pertinent continuum model variants but for which substantial improvements upon appropriate combinations are noted. Comparisons with results for (physically) similarly and differently based scales are likewise drawn and their differential statistics and parameters analyzed in terms of the variation in model components they reflect. Some possibilities of redundant inclusion of basic effects, such as electrical saturation, upon model combination are briefly considered.

Many results of dipolar solvation phenomena studies of the past 25 years have been correlated within a variety of empirical solvent polarity scales. In the recent course of defining a new scale, π, based on averaged solvatochromic shifts of $\pi \rightarrow \pi^*$ and $p \rightarrow \pi^*$ electronic transitions in substituted aromatics, good linear correlations could be demonstrated with at least eight of the earlier scales as well as internally among the various indicators.[1,2] The further observation that π varies roughly linearly with μ_v, the molecular dipole moment of select (i.e., aprotic, nonpolysubstituted aliphatic) solvents was taken to imply that specific interactions rather than bulk dielectric effects are major determinants of such solvation.[2,3] Equally good linear fitting could, however, be obtained by using a continuum reaction field model which although modified from the apparently unrealistic boundary and radial dependence conditions of Onsager nevertheless remains a bulk or many solvent molecule representation.

It is the purpose of the present study to attempt resolution of this apparent anomaly through reexamination of reasonable electrostatic models for solvent effect transmission, at least to the extent they might apply and be differentiable in the π- and related polarity scale measures. More firmly grounded theoretical formulations such as of the static and Langevin–Boltzman fields for molecular pair dipole–dipole interactions are considered, particularly for solvent in the near-neighbor region. The other, or uniform dielectric medium extreme as represented by the Onsager model is also reexamined, as are some modifications which incorporate various degrees of self-induced solvent molecule alignment. Common features to both, such as electrical saturation, are analyzed with particular attention to their abilities to blur distinctions among the extreme model types.

Theory: Models and Methods

Individual Solvent Dipole Effects. Of the two extreme views of dipolar solvation, the one presuming individual solute–solvent molecule interactions as dominant supposes knowledge of the spatial and, to the extent there are orientational changes with time, the temporal distributions of the interacting species. Models of the system are likewise conveniently characterized in terms of extremes, to wit, static and rotationally fluctuating point dipoles. The electric field along the dipolar axis of a solute molecule due to the presence of a static solvent molecule dipole located on an extension of this axis and making an angle θ_v with it produces the following reaction field[4a] (see Figure 1a).

$$\mathcal{F}_S = \left[\left(\frac{3\mu_v \cdot \mathbf{R}}{R^5}\right)R - \frac{\mu_v}{\mathrm{R}^3}\right]_{\cos\theta_u = 1} = (2\mu_v/R^3)\cos\theta_v = \kappa_v(kT/\mu_u)(2f) \quad (1)$$

However, if subject to thermally induced fluctuations of its (θ_v-dependent) orientation, the solvent molecule produces, by a variant of the familiar Langevin–Boltzmann analysis, the alternative average field[4b]

$$\mathcal{F}_R = (kT/\mu_u)(2f \coth 2f - 1) = (2\mu_v/\mathrm{R}^3)[\coth 2f - (1/2f)] \quad (2)$$

where $f = \mu_u\mu_v/R^3kT$, μ_u and μ_v are the dipole moments of the solute and solvent molecules, respectively, viewed as point dipoles, and R is the distance between them.

Since the electronic transitions and many other observables correlated by the scales of interest are functions of axial polarization in this, the principal solute dipole direction, and further, the most likely position to be occupied by a single solvent molecule is head (or tail) on to this dipole, i.e., $|\cos\theta_v| = |\kappa_v| = 1$, it is reasonable to expect the solvent polarity measure P to be proportional to one or the other of these reaction fields depending upon whether the averaging process can occur within the time scale of the observation.

$$P_v^{\,u} = A^u + B^u\mathcal{F}_v^{\,u} \quad (3)$$

If interactions among them are neglected, additional solvent molecules should contribute additively to the field along this original solute dipole axis, that is, $\mathcal{F}_v = \sum_i \mathcal{F}_{iv}$ and $\mathcal{F}(\theta) = \mathcal{F}(0)\cdot g(\theta)$, where θ is the angle of displacement of the solvent dipole from the solute axis (= θ_u, see Figure 1b and the Appendix). Assuming equal numbers and position (with respect to the solute) of participant solvent molecules for the variety of solvents whose effects define the scale, it appears appropriate therefore to seek correlation of the scale metric with $2f \coth 2f - 1$ and $2f$, respectively, depending upon whether or not thermal averaging pertains.

Therefore,

$$\begin{aligned} P &= A + B\cdot g\cdot\mathcal{F} \\ &= \alpha + \beta(2f\coth 2f) \\ &= \alpha' + \beta'(2f) \end{aligned} \quad (4)$$

where for a constant solute and temperature $f = C'\mu_v/[D + (3M_v/4\pi\rho_v)^{1/3}]^3$. C' and D are constants of the scale proportional, respectively, to the dipole moment of the solute divided by the temperature (= $C\mu_u/kT$), and to the radius of the solute molecule assumed spherical (C', it should be recognized, is capable of representing noncentral finite dipole position therein[4c]). The solvent is likewise assumed spherical and its radius, appropriate for touching-sphere representation of the interdipole distance, is

---

[†] Research carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

(1) M. J. Kamlet, J. L. Abboud, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 6027 (1977).

(2) J. L. Abboud, M. J. Kamlet, and R. W. Taft, *J. Am. Chem. Soc.*, **99**, 8325 (1977).

(3) J.-L. M. Abboud and R. W. Taft, *J. Phys. Chem.*, **83**, 412 (1979).

(4) (a) C. J. F. Böttcher, "Theory of Electric Polarization", Vol 1 2nd ed., revised by O. C. Van Belle, P. Bordewijk, and A. Rip, Elsevier, Amsterdam, 1973, p 18; (b) p 162; (c) p 152.

0002-7863/81/1503-6036$01.25/0 © 1981 American Chemical Society

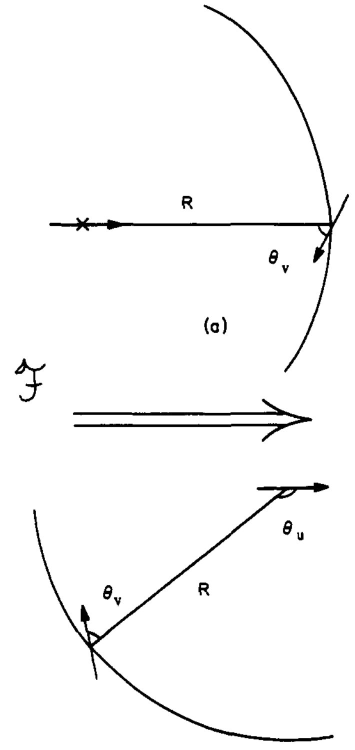

Figure 1. Reaction fields in the presence of (a) coaxial and (b) angularly (by θ_u) displaced solvent dipoles.

obtained from its molar volume and density, M_v and ρ_v, under the further assumption that these species in bulk are completely space filling. The calculation of R and notation follow a similar development for single on-axis dipolar fields recently applied to correlate solvent-induced ESR coupling constant shifts,[5] about which more later appears.

The extremum behavior of the function $2f \coth 2f$ is usefully examined at this point. Where f is large (strong dipoles and/or short interaction distance), this function goes as $2f$ to infinity, the same as the static dipole function. This behavior is certainly rational; heavy Boltzmann energy weighting would produce essentially "frozen" optimum configurations. Where f is small, the function goes as $(1/3)(2f)^2$ to unity, substantially different from the static function both in slope and limit. The former (large f) region is more likely in present cases where distances of separation of less than 10 Å and sizeable moments are typical. Appreciable alignment of the solvent molecules in the near neighborhood of solute is, as implied above, a manifestation of such interaction, properly characterized as solute-induced dielectric saturation. As a corollary, only through examination of solvent sets which include low-moment or nonpolar members should statistical distinctions between the individual molecule dipole models ever be possible.

Average Dipole–Bulk Medium Effects. Continuum models, on the other hand, recognize no solvent molecule enumerability, localization, or structure and in their simplest original form, Onsager's,[6] no difference in average orientation of solvent in regions close to or removed from the solute. The latter is reflected in a constant permittivity of the medium, commencing at the consequently well-defined solute–solvent boundary and continuing thereon out. Refinements have recently been introduced which remove the inherent boundary discontinuity while providing more physically realistic asymptotic behavior for the spatial permittivity approaching bulk values.[7,8] Such models are found to significantly if not universally improve correlations among such individual molecule properties as dipole moments and polarizabilities with bulk electrical properties, i.e., dielectric constant. Persistent deviations appear mainly to be due to specific molecular interactions in the liquid,[9,10] e.g., complexation, of which hydrogen bonding is a prime example, above and beyond those of the averaged solvent-induced dielectric saturation effects presumed to be the major physical factor reflected by the asymptotic permittivity modifications.

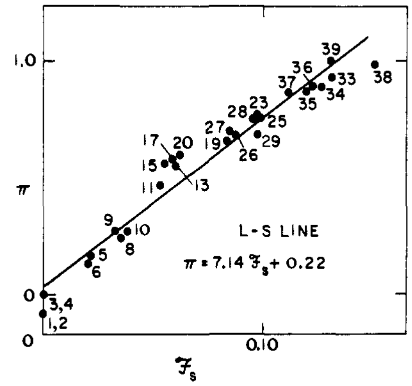

Figure 2. Select solvent π values vs. optimized $\mathfrak{F}_S$ values.

The four continuum models compared in ref 8 will to greater or lesser extents be examined here with reaction fields and polarity scales correlated through eq 3. The models and their associated fields and radial permittivity functions are as follows, for convenient reference.

$$\text{Onsager, } \phi_{\text{O}}\text{: } \epsilon = \epsilon_{\text{B}}$$

$$\text{Buckingham, } \phi_{\text{B}}\text{: } \epsilon = 1 + (\epsilon_{\text{B}} - 1)[1 - (a/r)^4]$$

$$\text{direct exponential, } \phi_{\text{DE}}\text{: } \epsilon = \epsilon_{\text{B}} - (\epsilon_{\text{B}} - 1)2^{-(r-a)/(2a)}$$

$$\text{inverse exponential, } \phi_{\text{IE}}\text{: } \epsilon = \epsilon_{\text{B}}{}^{1-a/r}$$

where ϵ_B is the bulk permittivity, a the radius of the spherical cavity containing the dipole at its center, and r ($\geq a$), the distance from this point. For $r < a$, the vacuum value of unity for ϵ pertains. Another model with inverse square exponential dependence, $\epsilon = \epsilon_B{}^{1-(a/r)^{1/2}}$ and field ϕ_{IRE} is also briefly examined, mainly because of its almost perfect mimicry of the reaction fields of a prototype structured solvent theory, i.e., of the Wertheim mean spherical model.[8,11] The reaction fields, ϕ, for the Onsager and inverse exponential models are obtainable analytically; for the others, numerical methods as outlined in ref 8 have been employed in their generation from the experimental bulk dielectric constants for each solvent.

Statistical fittings to eq 3 are by conventional linear least squares, but to eq 4, they are by Gauss–Newton successive approximation methods[12] because of the nonlinearities produced in the determination of C and D and by the coth function.

Results and Discussion

π* Scale. A number of the more revealing parameters and statistics obtained upon correlation of the π values for select solvents (π^*) with the individual dipolar interaction models are given in Table I. The appellation "select" and choices for inclusion in this group follow the conventions of the scale designers[1-3] to eliminate as well as possible other than purely dipolar solute–solvent interaction effects while maintaining a significantly populated scale with respect to both spread and distribution. There are 28 solvents in this set.

Several interesting features are quickly apparent. The first and of undeniable importance in the present context is the observation that the static dipolar field model fits the data well (see also Figure 2), while the Langevin–Boltzmann averaged field model does not

---

(5) A. H. Reddoch and S. Konishi, *J. Chem. Phys.*, **70**, 2121 (1979).

(6) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

(7) H. Block and S. M. Walker, *Chem. Phys. Lett.*, **19**, 363 (1973).

(8) S. Ehrenson, *J. Comput. Chem.*, **2**, 41 (1981).

(9) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

(10) H. Fröhlich, "Theory of Dielectrics", 2nd ed., Oxford University Press, London, 1958.

(11) M. S. Wertheim, *J. Chem. Phys.*, **55**, 4291 (1971).

(12) W. C. Hamilton, "Statistics in Physical Science", Ronald, New York, 1964, pp 150–156.

Table I. Individual Field Model π^*-Scale Correlations[a]

model	α	β	D	C^b	RMSD	r	other statistics[c,e]
$\mathcal{F}_S$	0.022	7.14	16.7		0.0642	0.9812	1, 2, $\overline{15}$, $\overline{17}$, $\overline{20}$, 38; $D_{95} > 7.2$
	0.049	0.485	[5]		0.0763	0.9733	1, 2, $\overline{15}$, 17, $\overline{19}$, 35; >99.5
	0.013	0.000_9[d]	[∞]		0.0734	0.9753	$\overline{15}$, $\overline{17}$, 19, $\overline{20}$, 38; >99.5
	0.141	0.024	[0]		0.1390	0.9084	>0.2; 1, 2, $\overline{19}$, 35, 37; >99.9
$\mathcal{F}_R$	0.041	0.092	2.2	[1.5]	0.1141	0.9393	>0.2; 1, 2, $\overline{19}$
	0.036	0.080	2.9	[2.5]	0.1047	0.9491	>0.2; $\overline{19}$
	0.030	0.067	4.0	[5]	0.0939	0.9593	>0.2; $\overline{19}$
	0.023	0.039	7.0	[25]	0.0770	0.9728	see $\mathcal{F}_S$ optimum
	0.029	0.053	3.5	[5]	0.0860	0.9670	set with pt 19 deleted
				Continuum $\mathcal{F}$			
Onsager	−0.690	1.596			0.0688	0.9783	$\overline{5}$, 10, 26, 29, $\overline{38}$, $\overline{39}$
+ polarization[f]	−0.519	1.451			0.0640	0.9813	same as unpolarized
Buckingham	−0.361	1.390			0.0610	0.9830	$\overline{5}$, 26, 29
dir exp	0.001	1.480			0.1008	0.9529	>0.15; 1, 2, 4, $\overline{13}$, $\overline{19}$
inv exp	−0.249	2.618			0.0708	0.9770	1, 2, $\overline{13}$, $\overline{19}$, 29
inv root exp	−0.190	3.863			0.0786	0.9717	1, 2, 4, $\overline{13}$, $\overline{15}$, $\overline{19}$

[a] Parameters as defined in eq 4 for individual dipolar fields and in eq 3 for continuum fields. When in brackets, these have been specified and held, otherwise optimized. RMSD and r are, respectively, the root-mean-square deviation and the multiple correlation coefficient. [b] $C = C'kT/\mu_u$; $T = 298$ K and μ_u assumed 5.4 D. For the static field $C = 1$ by definition. [c] Series of numbers specify which solvents, according to coding of Table I, ref 3, exhibit deviations $>d_M$. Here $d_M = 0.1$ unless otherwise specified. Bars indicate negative deviations, i.e., computed–observed < 0. [d] In units of D^3. [e] Subscripted parameter inequalities indicate range of the parameter values permissible, to the Cl implied by the subscript. Unaccompanied inequalities indicate the CL at which the line parameters may be rejected as equivalent generally, unless otherwise specified, to the optima for this model. [f] Polarization of the solute dipole leads to an Onsager reaction field proportional to $(\epsilon - 1)/(2\epsilon + \eta^2)$ rather than $(\epsilon - 1)/(\epsilon + 1)$, where η is the refractive index of the indicator solute. Assuming the average $\eta \sim\sqrt{2}$ produces the slightly different parameters but essentially identical fitting as for the unpolarized Onsager field.

for any reasonable value of the coth-scale factor, C. Only in the limit of increasing C, where the fluctuating and static dipole models converge, can good $\mathcal{F}_R$-field fitting be achieved. Examination of the major deviants suggests differentiation between the models depends importantly upon the presence of null-moment (nonpolar) members of the solvent set. This result is recognized as entirely consistent with the essentially instantaneous nature of the observations, i.e., UV spectroscopic measurement of solvatochromic shifts, with respect to rotations of the solvent dipoles.

The static field model fittings suggest a large interaction distance, D, characterizing the solute dipole (actually an average distance, considering the fact that the π scale is obtained from shift effects on a number of related aromatic molecular solutes). The optimum value, 16.7 Å, seems physically large but of only minor concern in light of the shallow least-squares dependence upon this parameter implied by $D_{95} > 7.2$ Å. The latter states that within the 95% confidence level (CL) of hypothesis testing, the conventional boundary of chance, the length 7.2 Å provides statistically indistinguishable fitting,[13] (i. e., $\mathcal{R}_{1,24,0.95} = 1.085$). On the other hand, $D = 5$ Å provides, to the 99.5% CL, a distinguishably poorer fit of the data than the optimum.

For D approaching infinity, that is, toward independence of the static model to the distances between the interacting dipoles, reasonably good fitting of the data is maintained, although distinguishably poorer, again to a high level of confidence (>99.5%), than the optimum. This limit, it should further be noted, corresponds to correlation against μ_v (see eq 4 and definitions, with $C' = 5.4 \times 48.566$ Å^{-3} D^{-1}), yielding α and $\beta C'$, respectively, as 0.013 and 0.236 and $r = 0.975$ and thereby verifying and rationalizing the correlation between μ and π^* previously reported.[3,14]

The other extreme, that is where D is zero and the field and hence π^* are presumed linearly dependent upon $(\mu\rho/M)_v$, provides a much poorer correlation than any other model considered, including the fluctuating dipole. On these as well as the obvious physical grounds, no further attention will be paid this limit.

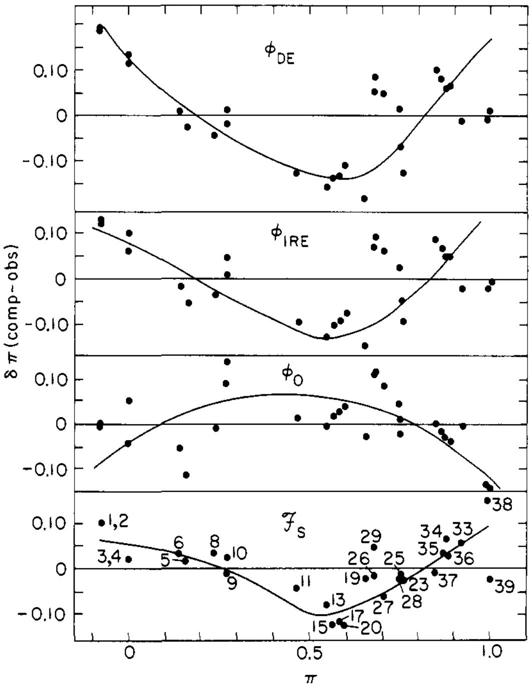

Figure 3. Least-squares deviations for π fitted to various reaction fields as functions of π. Solvent numbers as in Table I, ref 3. The curves here and in the other least-squares deviation figures are sight drawn solely for the purpose of indicating trends. It should likewise be recognized that curvature in these plots is in the opposite sense from those where solvent scale fitting as a function of field is displayed, i.e., where the latter is concave downward, as in Figure 2, it is upward here, and vice versa.

The correlations with the continuum fields are no less interesting. While there is obvious curvature in the linear fitting of π^* to the Onsager field, a fact noted previously (see, e.g., Figure 6 of ref 3), the statistics for the unconstrained correlation indicate it *not to be distinguishably poorer than the static individual dipole field model* (viz., $F_{26,25,\alpha} = 1.104$, or $\alpha < 60\%$). In fact, it appears to be slightly better, with only one—and hardly a significant one—exception, than any other continuum field correlation tested. This conclusion is at variance with earlier analysis,[2] which may not, however, have been predicated solely on the effects of the select solvent group.

In contrast to the apparent curvature of the Onsager field plots, when correlation is against the modified fields the curvature is

---

(13) S. Ehrenson, *J. Org. Chem.*, **44**, 1793 (1979).

(14) The small differences are doubtless due to the slightly different values chosen for the moments of solvents 35 and 37 (both by −0.3 D) and 19 (by +0.2 D), following McClellan's updates.[15b]

(15) (a) A. L. McClellan, "Tables of Experimental Dipole Moments", Vol. 1, W. H. Freeman, San Francisco, 1963; (b) Vol. 2, Rahara Enterprises, El Cerrito, CA, 1974.

Table II. Combined Field Model π^*-Scale Correlations[a,c,e]

$\mathcal{F}_S$ + continua	α	β_S	D	B_C	RMSD	r	other statistics
Onsager	−0.343	7.08	21.2	0.782	0.0380	0.9934	none; $D_{95} > 7.8$
	−0.384	0.000_9[d]	[∞]	0.862	0.0408	0.9925	none; >$\underline{92}$.5
	−0.551	0.005	[0]	1.298	0.0605	0.9833	10, 29, $\overline{38}$; >99.9
Buckingham	−0.216	1240	143	0.810	0.0450	0.9908	none; $D_{95} \geq 10.5$
dir exp	0.028	11.4	14.8	−0.105	0.0641	0.9812	$\underline{1,\ 2,\ \overline{15}}$, $\overline{17}$, $\overline{20}$, 38
inv exp	−0.137	0.000_8[d]	∞	1.394	0.0559	0.9858	$\underline{\overline{15}}$, $\underline{\overline{17}}$, $\underline{20}$
inv root exp	−0.092	0.001_0[d]	∞	1.794	0.0602	0.9835	$\overline{13}$, $\overline{15}$, $\overline{17}$, 20

combination F tests[b]	Onsager	Buckingham	dir exp	inv exp	inv root exp
overall	942	669	324	430	369
$\mathcal{F}_C$ after $\mathcal{F}_S$	46.8	37.2	0.2	18.2	12.2
$\mathcal{F}_S$ after $\mathcal{F}_C$	56.8	20.8	36.8	15.2	17.6
r(part)[f] $\mathcal{F}_S$–π	0.83	0.67	0.77	0.62	0.64
$\mathcal{F}_C$–π	0.81	0.77	−0.08	0.65	0.57
$\mathcal{F}_S$–$\mathcal{F}_C$	−0.36	−0.07	0.68	0.18	0.24

[a] Same as footnote *a*, Table I. [b] Variance ratio tests of Fisher-Snedecor type, see ref 18. [c–e] Same as footnotes *c–e*, Table I. [f] Partial correlation coefficients.

Table III. E_T-Scale Reaction Field Correlations[a]

model	α-30	β	D	C[b,f]	RMSD	r	other statistics[c,e,g]
$\mathcal{F}_S$	2.066	1.61	1.973		0.6604	0.9885	$\overline{26}$, 38; $3.48 > D_{95} \geq 0.97$
	1.027	0.332	[0]		1.027	0.9718	> 1.5; $\overline{26}$, $\overline{35}$, $\overline{36}$, $\overline{3E}$; >99.9
	1.712	0.012[d]	[∞]		1.763	0.9146	> 1.5; 8, $\overline{35}$, $\overline{37}$, 3E, 38; >99.9
$\mathcal{F}_R$	2.064	1.28	1.599	[1]	0.6956	0.9872	8, $\overline{26}$, $\overline{3E}$, 38
	2.068	0.777	1.912	[2]	0.6634	0.9884	$\overline{26}$, 38
Onsager	−13.710			28.33	1.666	0.9241	>2; $\overline{6}$, $\overline{35}$, $\overline{37}$, 1E, 3E, 5E
+ $\mathcal{F}_S$	−2.194	0.743	1.182	7.36	0.5049	0.9933	none; $C/S = 17$, $S/C = 178$
Buckingham	−6.150			22.32	1.304	0.9542	>2; $\overline{6}$, $\overline{35}$, $\overline{37}$, 3E
+ $\mathcal{F}_S$	−0.867	0.485	0.802	7.88	0.4728	0.9941	none; $C/S = 29$, $S/C = 19$
dir exp	0.984			20.84	0.9990	0.9734	≥2; 3E
+ $\mathcal{F}_S$	1.664	0.174	0.019	10.99	0.5049	0.9933	$\overline{13}$; $C/S = 55$, $S/C = 52$
inv exp	−3.465			39.35	1.055	0.9703	≥2; $\overline{37}$, 3E
+ $\mathcal{F}_S$	−0.531	0.216	0.159	19.36	0.4684	0.9942	$\overline{13}$; $C/S = 59$, $S/C = 73$
inv root exp	−2.305			56.84	1.022	0.9721	≥2; $\overline{37}$, 3E
+ $\mathcal{F}_S$	−0.235	0.072	−0.633	33.40	0.5529	0.9919	$\overline{13}$, 3E
	0.281	0.194	[0]	25.85	0.5779	0.9912	13, 3E; <80; $C/S = 24$, $S/C = 38$

[a,b] Footnotes of Table I pertain. [c] Here $d_M = 1$ unless otherwise specified. Other specifications of footnote *c*, Table I, pertain. Solvents coded with E are noted in the text. [d,e] Same as footnotes *d* and *e*, Table I. [f] In the continuum and combined model fittings this parameter is B_C. [g] *C/S* and *S/C* are, respectively, the variance ratio tests for application of the continuum after the static field and vice versa (see Table II).

generally concave downward and more obviously, as one might reasonably expect, the poorer the linear fitting (see Figure 3 and compare Figure 5 of ref 3). In this regard, the modified continuum correlations resemble those against $\mathcal{F}_S$, although some important differences in the outlying points determining the curvature are to be recognized. Furthermore, it is particularly noteworthy that the permittivity modification which most closely mimics the field behavior of structured (MSM) solvent provides no better (in fact, generally worse) linear representation of the π^* scale.

Introduction of radial permittivity variation into the Onsager function appears, at least operationally, to accomplish much the same result as is achieved through use of the individual dipole interaction mode. It becomes a matter of interest then in light of earlier attributions to saturation to inquire as to the result of applying the effects, single dipole and continuum together. Precedent exists for combination of reaction field components involving higher order poles;[16] this is not what is proposed here. Ther results of various $\mathcal{F}_S$, $\mathcal{F}_C$ combinations are to be found in Table II. These are always correlationally superior to combinations with $\mathcal{F}_R$, as the earlier individual field results and interpretations implied they would be.

Substantial improvement over either single model fitting is obtained with $\mathcal{F}_S$ and Onsager fields combined. Comparisons to either alone indicate to >99.9% CL the statistical significance of the presence of the other field ($\mathcal{R}$ values, respectively, 1.689 and 1.811 where $\mathcal{R}_{b,24,0.999} = 1.259, 1.334$, for b of 1 and 2[13]). The roughly equal values obtained in the combination F tests likewise support the contention of important contributions from each field. (Individual F values for either field alone, obtainable from the individual field correlation coefficients, viz., $F = (n - b)r^2/(1 - r^2)$, where b is the number of fitted parameters, are also roughly equal, i.e., 580 for $\mathcal{F}_C$ and 646 for $\mathcal{F}_S$).

The root-mean-square deviation (RMSD) of 0.0380, corresponding to σ of 0.041 (with 24 degrees of freedom), yields an f value of 0.06 (or an Exner[17] ψ value, perhaps more appropriate here because of intercept freedom, of 0.11). These certainly constitute acceptable measures of overall fit by most criteria. As before, the optimum solute interaction radius, D, is predicted to be rather large, but also, as before, the error dependence is shallow (i.e., $D_{95} > 7.8$ Å), implying an entirely reasonable range of interdipole distances. Confidence that D is the optimum value rather than infinity is somewhat weaker than in the individual static dipole fitting (here >92.5%).

Not surprisingly, such great improvements in fitting are not generally noted when the modified continuum and $\mathcal{F}_S$-field models are combined. The Buckingham field fitting is bettered substantially ($\mathcal{R} = 1.356$, likewise significant to the 99.9% CL) but considerably less than was the unmodified field fitting. Much less improvement is noted for the other continuum modifications,

---

[16] R. J. Abraham and M. A. Cooper, *J. Chem. Soc. B*, 202 (1967); R. J. Abraham and Z. L. Rossetti, *J. Chem. Soc., Perkin Trans. 2*, 582 (1973).

[17] O. Exner, *Collect. Czech. Chem. Commun.* **31**, 3222 (1966).

with essentially none for the direct exponential field.

These results are readily rationalized in terms of complementarity on the one hand, i.e., where the $\mathcal{F}_S$-field model provides appropriate radially dependent solute–solvent ordering to the radially independent Onsager dielectric, and redundancy on the other to greater or lesser extents where the continuum functions have been modified empirically to take such near-neighbor ordering into account. This conclusion finds further support in the partial correlation coefficients between the independent variables $2f$ and ϕ, easily extracted in the course of least-squares fitting. Only for the ϕ_{DE} and the static field, $r = 0.68$, are the variables clearly and positively correlated (to much greater than the 99% CL[18]). For ϕ_O and ϕ_B, characterized by r values, respectively, of −0.38 and −0.07, they probably are not (<95%). Moreover, the negative sign of the coefficients suggests redundancies in composite effects are not of concern in these cases. The inverse exponential fields are likewise correlated with the static dipolar field only weakly if at all, but here what overlap exists is positive (r for ϕ_{RE} and ϕ_{IRE} with $2f$ is, respectively, 0.18 and 0.24). Other measures may also be cited to support the conclusion and thereby to render more unlikely the hypothesis of chance improvement. Suffice it to say at this point that the saturation effects introduced by the specific dipole fields improve continuum representation of the π^* scale to well beyond what internal corrections for these effects through permittivity modification can accomplish. Distinctions between solute- and solvent-induced saturation may indeed be meaningful, at least in the present context, but the reversal in goodness-of-fit ordering of the combined continuum fittings compared to the individual continuum fittings also seems to suggest variable component redundancies.[19]

E_T Scale. The foregoing results and conclusions concerning electrical effects operative in the π^* scale may be subjected to interesting generality tests by similarly patterned examination of other polarity scales. One is chosen here, the $E_T(30)$ scale,[23] henceforth called E_T, a significantly spread and populated scale which has been extensively used in a variety of correlations.[24] Discussions of the similarities to and differences from the π^* and other scales may be found elsewhere.[11]

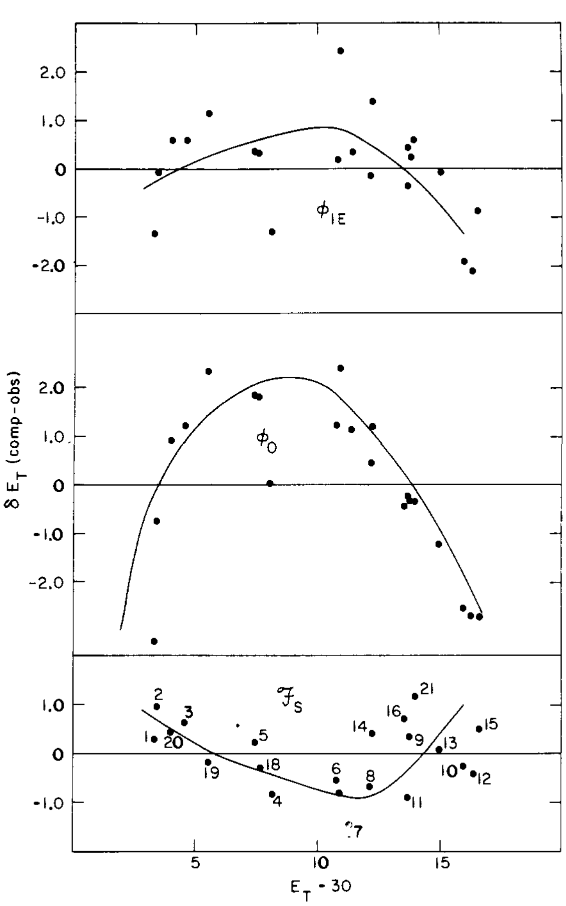

Figure 4. Least-squares deviations for E_T fitted to various reaction fields as functions of E_T. Solvent numbers serially as presented in ref 24.

Table III, constructed as a combination form of Tables I and II, immediately reveals perhaps the most important similarity between the E_T and π^* fittings. As with π^*, fitting to the static field is always better than to the fluctuating dipolar field for any finite scale factor C, although the difference in quality is much less severe for any physically reasonable choice of this factor. This appears to corroborate the conclusions concerning observational time scales previously drawn.

The solute radius obtained as a best fit is considerably smaller here, perhaps surprisingly, considering the size of betaine, 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide, upon whose solvatochromic shifts the E_T scale is based. Too much importance should not, however, be made of this difference considering where the dipole center might be expected to lie (near the periphery rather than at the molecular center) and the relative softness of this statistically optimized parameter, i.e., $D_{95} < 3.5$ Å. At the same time, greater confidence in differences from the extremum models ($D \rightarrow 0$, $D \rightarrow \infty$) than in the π^* correlations is indicated.

For the most part, other comparisons also support the major conclusions derived from the π^*-scale analysis, with some important differences. For example, a distinct change in order of correlation ability among the continuum fields is noted, e.g., here the direct exponential function is best and the Onsager worst. Moreover, all the exponential permittivity modified fields are of similar quality and all are considerably poorer than the $\mathcal{F}_S$ field. The difference, static compared to continuum field fittings, is substantially greater here; the former is statistically superior, to 95% CL, to *any* of the latter. This is clearly indicated by the relative ranges of deviations displayed in Figure 4. The deviation trends in this figure also suggest, at least for the E_T scale and in contrast to the π^* fittings, that permittivity modifications do not overcompensate for the Onsager model deficiencies.

But considerably more important, when combined, significant improvement over the individual model results are generally ob-

---

(18) G. W. Snedecor and W. G. Cochran, "Statistical Methods", 6th ed., Iowa State University Press, Ames, IA, 1967, Section 13.8.

(19) Subsequent to initial submission of this paper, two rather similar analyses of the π scale have appeared which introduce solvent polarizability terms explicitly to linear dipole moment[20] and (Onsager) reaction field[21] functions, respectively, with the claimed effect of improving as well as generalizing in scope the correlations forthcoming (contrast to solute polarizability effects explored in Table I). Bekárek introduces the factor $(\eta^2 - 1)/(2\eta^2 + 1) = f(\eta^2)$ multiplicatively, where η is the refractive index, producing an equivalent of the cross-term of the Buckingham IR shift equation.[22] Taft et al. use what they label as a reducing function, $P = [f(\eta^2) - 0.19][1 - 0.23\mu]$, additively, in a bilinear form, to a μ term. While a broader range of solvents, (particularly aromatic and polyhalogenated species) may, as claimed, be rationally accommodated by these modified forms—despite the physcially disquieting acceptance of (a) perturbative second-order (cross-) terms, to the neglect of those of first order, (b) isotropically averaged rather than directional measures of polarizability, (c) functions which have unrealistic (small η) limits, (d) several fitting parameter and statistical mismatchs among solvent groups, and (e) unexplained exclusions of a variety of solvents from the bilinear fitting—it appears entirely unlikely that such modifications or any simple variants can significantly improve the original π^*-set correlations. In fact, in fitting against the original π^* values (as displayed in Figure 5 of ref 3, to which ref 21 explicitly refers), the $f(\epsilon,\eta^2)$ provides slightly *poorer* statistics than does the Onsager field function along [i.e., $f(\epsilon)$]. With subsequently modified values, principally for CH_3CN (to 0.71), the advantage is shifted to the modified function, but only marginally (viz., $F_{26,26,\alpha} = 1.593$ or $\alpha <$ 90%). Because the identifies of the solvents used in the bilinear correlations are not completely obvious, similar comparisons are not easily drawn there. However, it seems certain from examination of Figure 8[20] that the nonchlorinated aliphatic solvents are more poorly fitted than by any one of several simple dipolar functions previously explored.

(20) R. W. Taft, J.-L. M. Abboud, and M. J. Kamlet, *J. Am. Chem. Soc.*, **103**, 1080 (1981).

(21) V. Bekárek, *J. Phys. Chem.*, **85**, 722 (1981).

(22) A. D. Buckingham, *Proc. R. Soc. London, Ser. A*, **248**, 169 (1958).

(23) C. Reichardt, *Liebigs. Ann. Chem.*, **752**, 64 (1971), and references given therein.

(24) Reasonable, if not as restrictive, care to exclude solvents which may interact by other than purely dipolar means has also been exercised here. To solvents 6, 8–10, 13, 17, 25, 26, 29, 33–39 of the π^* set (see Table I of ref 3 for their identity) are added propylene carbonate (1E), nitroethane (2E), hexamethylphosphoramide (3E), ethyl iodide (4E) and piperidine (5E). The same dipole moment changes for 35 and 37 are made as previously and the value of 4.3 D taken for HMPA (3E).

Table IV. Correlations of a_N for Di-*tert*-butyl Nitroxide with Classical Reaction Fields[a,h]

model	α-15	β	D	C[b,f]	RMSD	r	other statistics[c,e,g]
$\mathcal{F}_\mathrm{S}$	0.2352	0.050	0.927		0.04218	0.9559	1, $\overline{4}$, $\overline{13}$
	0.2526	0.022	[0]		0.04458	0.9506	1, $\overline{13}$, 20; $\leq$90.0
	0.2293	0.000_7[d]	[∞]		0.07499	0.8528	1, 2, $\overline{4}$, 9, $\overline{13}$, $\overline{20}$, $\overline{23}$; >99.9
$\mathcal{F}_\mathrm{R}$	0.2260	0.049	0.869	[1]	0.04221	0.9558	1, $\overline{13}$
	0.2308	0.033	0.990	1.63	0.04196	0.9564	1, $\overline{13}$
	0.2321	0.027	1.007	[2]	0.04198	0.9563	1, $\overline{4}$, $\overline{13}$
Onsager	−0.1747			0.786	0.07540	0.8510	$\geq$1; $\overline{4}$, 9, 10, $\overline{22}$, $\overline{23}$
+ $\mathcal{F}_\mathrm{S}$	0.1946	0.038	0.679	0.074	0.04193	0.9564	$\overline{4}$, $\overline{13}$; $C/S = 0.4$, $S/C = 45$
dir exp	0.1953			0.661	0.05803	0.9147	>1; 9, $\overline{23}$
+ $\mathcal{F}_\mathrm{S}$	0.2317	0.036	0.642	0.074	0.04209	0.9561	1, $\overline{4}$, $\overline{13}$; $C/S = 0.3$, $S/C = 18$
$\mathcal{F}_\mathrm{S}$	0.2070	0.068	1.259		0.03463	0.9715	none; $\delta_4 = 0.099$, $\delta_{13} = 0.097$
$\mathcal{F}_\mathrm{R}$	0.2025	0.056	0.981	[1]	0.03629		
	0.2080	0.031	1.119	[2]	0.03502		
	0.2076	0.022	1.203	[3]	0.03473		
Onsager	−0.2898			0.911	0.07031	0.8767	>1; 9, 10, $\overline{22}$, $\overline{23}$
+ $\mathcal{F}_\mathrm{S}$	0.1265	0.043	0.819	0.141	0.03369	0.9731	none; $C/S = 1.5$, $S/C = 60$

[a,b] Footnotes of Table I pertain. [c] Series of numbers specify which solvents according to coding of Table I, ref 5 exhibit deviations $>d_M$. Here $d_M = 0.07$ unless otherwise specified. Bars indicate negative deviations. [d,e] Footnotes of Table I pertain. [f,g] Footnotes of Table III pertain. [h] Upper rows of the Table with all 23 of the polar solvents of ref 5 employed in the fittings. In the lower rows, solvents 4 and 13, toluene and pyridine have been deleted.

tained, and again the most dramatic improvement is in the Onsager field results (combined compared to continuum fittings). All improvements are significant to >97.5% CL (with respect to the static field fitting). Interestingly, the structured solvent mimic, that is ϕ_{IRE}, provides the poorest results in combination and a completely unreasonable negative D value upon optimization (once again, this error mode is soft; hence physical attribution is unwarranted). The conclusion which does seem to emerge, however, is, again, that saturation corrections exercised through individual dipolar interaction effects on the reaction field promote significantly improved correlation of the E_T scale by continuum fields. In fact here, if either is to be used alone, the static field component is much preferred.

Other Scales. The nitrogen hyperfine coupling constant shifts in di-*tert*-butyl nitroxide due to solvent have been included in various cross comparisons with solvent polarity scales,[2,25] as well as being the subject of a recent study similar to the present.[5,26] It is of interest to reexamine these a_N fittings and the analytic results obtained by Reddoch and Konishi as contrasts to those above, both based upon UV electronic transition effects. The same set of 23 solvents they employed is examined; from various checks made it is presumed that similar if not identical physical property data such as dipole moments have been used. Unfortunately, several members are not of the previously "select" category; their exclusion, however, was considered to be more disadvantageous in the scale contraction sense than their retention threatened to be.

From Table IV it may be quickly gathered that, unlike the π^* and E_T cases, the a_N data are at least as well fitted by the $\mathcal{F}_\mathrm{R}$ as the $\mathcal{F}_\mathrm{S}$ field. The optimum values of $D = 0.97$ and $C = 1.5$ agree remarkably well with those previously reported (respectively, 0.92 and 1.4), particularly in light of the extraordinary shallow nature of the error surface. That the static field fits almost as well is a further reflection of the shallowness of this surface along the C coordinate. Physically this may be attributed to approach of all or most statistically important data to the large f limit for the $\mathcal{F}_\mathrm{R}$ fields appropriate to the (long) time scale of the observation. It should, however, be noted that conclusions concerning the large f limit are lent a degree of uncertainty by the lack of null- and small-dipole moment solvents (there are only two with moments less than 1 D, one of which is patently nonselect, toluene), and, further, that both small moment solvents are among the three worst deviators in all fittings tried. In fact, removal of the two worst negative deviators (computed minus observed), toluene and pyridine, both unquestionably nonselect, obliterates the error minimum along the C coordinate entirely. The $\mathcal{F}_\mathrm{S}$ and $\mathcal{F}_\mathrm{R}$ fittings remain, however, essentially equivalent at all C values. Nevertheless, significant differences from the previous correlations appear likely.

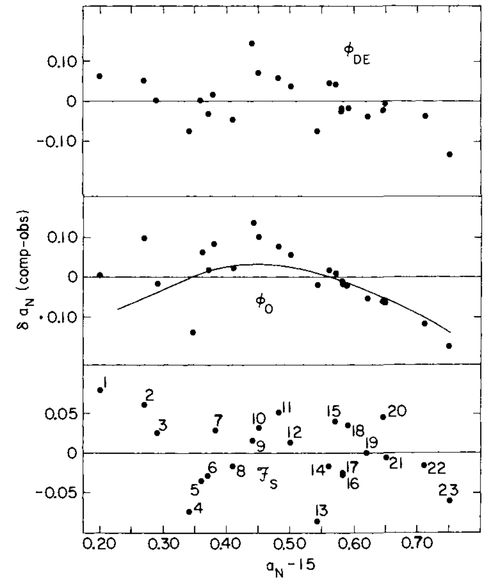

Figure 5. Least-squares deviations of a_N fitted to various reaction fields as function of a_N. Solvent numbers as in Table I, ref 5.

This conclusion is further supported by the results on fitting to the individual continuum reaction fields and in combinations with $\mathcal{F}_\mathrm{S}$. Combinations with $\mathcal{F}_\mathrm{R}$ are not reported; they are expected to be similar because of the similarity in $\mathcal{F}_\mathrm{S}$ and $\mathcal{F}_\mathrm{R}$.

As in the E_T correlations, the individual dipolar field fitting appears superior to any continuum field fitting, compared individually, but certainly less significantly so (e.g., 90% CL, comparison to direct exponential variant, which is, as in the E_T correlation, the best of the continuum group).[27] What is more

---

(25) B. R. Knauer and J. J. Napier, *J. Am. Chem. Soc.*, **98**, 4395 (1976).

(26) In fact, in ref 5, p 2129, brief mention is also made of a correlation of E_T for 14 solvents (unspecified) against individual dipolar fields with $D = 0$, presumably in the $\mathcal{F}_\mathrm{S}$ limit. The correlation coefficient 0.971, the only statistic given, compares well with the corresponding r value given in Table III. In ref 20, some results of bilinear polarizability–dipole moment correlation of the E_T scale, quite similar to those obtained for the π scale[19] are also briefly discussed.

(27) This comparison, it should be noted, suggests very much less confidence in rejecting the hypothesis of no difference between models than presented in ref 5. In fact, if the 95% level defines the chance limit, it cannot be confidently rejected.

striking though is the fact that in combination, *no significant improvement* is noted over the $\mathcal{F}_S$ fitting for any continuum field variant, an entirely different result than was obtained for the π^* and E_T solvent scales. Moreover, this result is not affected by the presence or absence of the two nonselect solvents which were discussed before in connection with the $\mathcal{F}_S$ and $\mathcal{F}_R$ fittings.

Rationalization of this lack of improvement may be found in the plots of a_N vs. the individual dipole and continuum fields presented, respectively, in Figure 5 and, e.g., Figures 2 and 1 of ref 5. Unlike the corresponding π^* and E_T cases, the deviations distribute essentially randomly about the least-squares lines without the tendencies toward compensation of the individual dipole and continuum field curvatures. There is in fact no discernible curvature in the $\mathcal{F}_S$ fitting and the very slight tendency which may be detected in the primitive continuum function correlation essentially disappears when the modified functions are used. Whether any of these fitting differences, scatter or individual fittings, have meaning in the context of physical differences between a_N and other "true" solvent scales as probes of the solvent on a microscopic level, as suggested by Knauer and Napier, proponents of an a_N-solvent scale,[25] is not, however, apparent at this time.

It could be profitable to examine others of the wide variety of polar solvent scales in similar ways. Possibilities exist there of uncovering systematic details on best-fitting single fields, field combinations and structural components as functions of substrate, probe site and physical property observed. Best chances to obtain parallel results to those reported appear to lie with those scales based on similar observables and which correlate (inter-scale) strongly. Conversely, differences in kind (field types, structure) may well be forthcoming from those scales which exhibit poor or perhaps even moderate quality correlations with π^*, E_T, or a_N.[28]

Conclusions

On the basis of conventional linear fitting statistics alone, correlations of the π^* scale of solvent effects by the most primitive continuum field and those reflecting individual dipolar interactions are found to be of remarkably similar quality. Furthermore, there seems to be no improvement in correlational ability accompanying improvement in the continuum model to account for radial permittivity variations of the solvent. Upon combination of the individual dipole and continuum fields, however, particularly for the least sophisticated of the latter, substantial improvement is noted. This is consistent with observations of curvature in the individual field plots not recognized by the simple statistics and may be taken to suggest that such specific field effects as electrical saturation, exercised through near-neighbor solvent molecule alignment in the individual dipolar models, serve as better modifiers of important deficiencies than can be easily accomplished within the continuum models. A corollary is that a certain degree of redundancy may be introduced if the improved continuum models are employed in the combinations, which may worsen correlational ability.

From considerations of the E_T as well as π^* scales, both based on essentially instantaneous observations, the expected superiority of a static to fluctuational dipolar field model could be demonstrated, although how these might become indistinguishable (in the high moment, short interaction distance limit) was also recognized. Excluding the fact that the individual dipole field model appeared significantly superior to those for continua only in the E_T correlations, major differences in kind between the E_T and π^* scale were not apparent, at least for the restricted solvent set examined.

Comparison to solvent effects on a_N values (nitrogen hyperfine coupling constants) of di-*tert*-butyl nitroxide, did, however, reveal important differences. For these data, no improvement over the individual dipolar field accrued upon combination with continua, and moreover, the fluctuational rather than the static field seemed more potent correlationally. Explanation of the former may be found from structural considerations, i.e., the electron involved being strongly localized in the nitroxide bond which is close by to one solvent at the O end of the molecule but strongly insulated by the alkyl groups to the rear. The latter should hinge mainly on the time required for the observation, slow enough to accomodate rotational averaging of the configuration of this presumed coaxially located single solvent molecule, and in obvious contrast to the essentially instantaneous observations on more fully solvated species characterizing the other scales discussed. Differences among the various scales in geometric and steric requirements for near-neighbor solvent location are likewise acknowledged for their potentials to cause differences in correlational quality.

Appendix

The energy of interaction of two dipoles separated by a distance R and oriented, respectively, at angles $\theta_u\phi_u$ and $\theta_v\phi_v$ to the vector connecting them is[29]

$$W = -\mu_u\mu_v[2\cos\theta_u\cos\theta_v - \sin\theta_u\sin\theta_v\cos(\phi_u - \phi_v)]/R^3 = -\mu_u\mu_v A_{uv}/R^3 \tag{A1}$$

The reaction field along the axis of u (which with the vector **R** is taken to define the reference plane and hence ϕ_u), produced by v, Boltzmann averaged over its angular orientations may be written, therefore, as

$$\mathcal{F}_R = \frac{\dfrac{\mu_v}{R^3}\displaystyle\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} A_{uv}e^{-W/kT}\,d\phi\,d\theta}{\displaystyle\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} e^{-W/kT}\,d\phi\,d\theta} \tag{A2}$$

Angular subscripts for v are here and henceforth suppressed. Making the substitution $-W/kT = fA_{uv}$ and separating the denominator into θ and ϕ integrals yields

$$D = \int_0^{\pi} e^{2f\cos\theta_u\cos\theta}\sin\theta\,d\theta\int_0^{2\pi} e^{-f\sin\theta_u\sin\theta\cos\phi}\,d\phi \tag{A3}$$

which may be successively integrated to (6.412.6, 6.407, 6.457), (3.227.3, 6.477)[30]

$$D/\pi = \int_0^{\pi} e^{2f\cos\theta_u\cos\theta}J_0(if\sin\theta_u\sin\theta)\sin\theta\,d\theta \tag{A4}$$

$$= \sum_{l=0}^{\infty}\frac{(f\sin\theta_u)^{2l}}{4^l(l!)^2}\int_0^{\pi} e^{2f\cos\theta_u\cos\theta}\sin^{2l+1}\theta\,d\theta \tag{A5}$$

$$= \sum_{l=0}^{\infty}\frac{(\tan^2\theta_u)^l}{2^{4l}l!\,w}W_l(w) = 2\sum_{l=0}^{\infty}\frac{(\tan^2\theta_u/8)^l}{l!}V_l(w) \tag{A6}$$

where

$$W_l(w) = (-1)^{l+1}e^{-w}\sum_{k=0}^{l}\frac{(l+k)!\,(2w)^{l-k}}{k!(l-k)!} + e^{w}\sum_{k=0}^{l}\frac{(-1)^k(l+k)!\,(2w)^{l-k}}{k!(l-k)} \tag{A7}$$

$$V_l(w) = w^{2l}\,d^l(\sin w/w)/(w/dw)^l \tag{A8}$$

and $w = 2f\cos\theta_u$.

For the latter, the following useful recurrence relationships may be derived (6.472, 6.473)

$$d(wV_l)/dw = w^2V_{l-1} \tag{A9}$$

$$V_{l+1} = w^2V_{l-1} - (2l+1)V_l \tag{A10}$$

The double integral of the numerator, it may be quickly verified, is just the partial derivative of the denominator with respect to

---

(28) Table II of ref 2 contains information pertinent to this point, subject to careful interpretation. The scales are not as parallel as the correlation coefficients might be taken to imply. For example, only G vs., respectively, E_T, log k, S, and χ_R and S vs. log k and a_N vs. μ are within the 0.1 Exner ψ range, and all have 7 or less common members. G and P vs. π^* and P vs. E_K are within the 0.15 range but are somewhat more highly populated. Where the greatest mutality of subject solvents is in fact found is where ψ values range around 0.20, certainly not representative of high precision linear correlation.

(29) See F. London, *Trans. Faraday Soc.*, **33**, 8 (1937).

(30) Numbers in parentheses are equation references, relating to the derivation steps following, to be found in I. M. Ryshik and I. S. Gradstein, "Tables of Series, Products and Integrals", VEB Deutscher Verlag der Wissenschaften, Berlin, 1957.

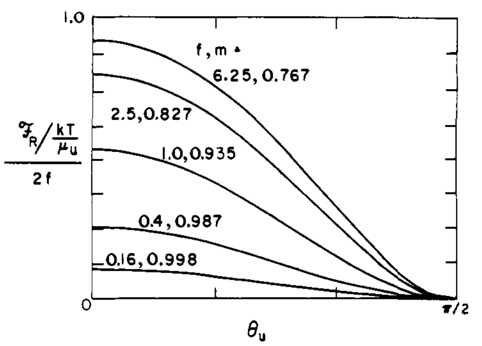

Figure 6. Variation of the Langevin–Boltzmann field as functions of the dipolar interaction parameter, f, and the solute axis displacement angle, θ_u. Parameters, m, are for fitted functions, $\mathcal{F}_R(\theta) = \mathcal{F}_R(0)\cos^{2m}\theta$; see Appendix.

f, or from eq A5 recognizing that the corresponding even sin θ integrals vanish

$$N = \frac{\mu_v}{R^3}\left[2\pi\sum_{l=0}^{\infty}\frac{(f\sin\theta_u)^{2l}}{4^l(l!)^2}\frac{\partial}{\partial f}\int_0^{\pi}e^{2f\cos\theta_u\cos\theta}\sin^{2l+1}\theta\,d\theta\right] \tag{A11}$$

This integral, also a Bessel function of imaginary argument, but of half-integer index conventionally labeled as $I_{l+1/2}$, is well characterized as regards recurrence relationships both for index raising and differentiation (6.496.4). Some algebraic manipulation thereafter yields the following forms, reasonably similar to those obtained for the denominator

$$\frac{NR^3}{\pi\mu_v} = \frac{1}{f}\sum_{l=0}^{\infty}\frac{(\tan^2\theta_u)^l}{2^{4l}\,l!\,w}W_{l+1}(w) = \frac{2}{f}\sum_{l=0}^{\infty}\frac{(\tan^2\theta_u/8)^l}{l!}V_{l+1}(w) \tag{A12}$$

Therefore

$$\mathcal{F}_R = \left(\frac{2\mu_v}{R^3(2f)}\right)\frac{\sum_{l=0}^{\infty}(\tan^2\theta_u/8)^l V_{l+1}(w)/l!}{\sum_{l=0}^{\infty}(\tan^2\theta_u/8)^l V_l(w)/l!} \tag{A13}$$

These series, rapidly convergent for small $\tan^2\theta_u$ (i.e., where the solvent molecule lies close to extensions of the solute molecule dipolar axis, and moderate sized f), are appropriate for most physical situations. Where $\tan^2\theta_u$ is large, alternative more rapidly convergent series may be derived through expansion of the exponential in eq A5, integration thereof, followed by recognition that the series produced are hyperbolic sine and cosine representations. The result is

$$\mathcal{F}_R = \left(\frac{2\mu_v}{R^3}\right)\left(\frac{2}{f}\right)\cot^2\theta_u\frac{\sum_{l=0}^{\infty}(2\cot^2\theta_u)^l V_{l+1}(w')/l!}{\sum_{l=0}^{\infty}(2\cot^2\theta_u)^l V_l(w')/l!} \tag{A14}$$

where $w' = f\sin\theta_u$. The alternative series are seen to become equivalent where $\tan^2\theta_u = 4$ or $\theta_u = 63.4$ or 116.6°. One or the other is found to suffice for all physically realizable cases; that is, less than 10 terms necessary for 1 part in 10^{-4} sum convergence for $f \leq 6.25$.

The dependence of $\mathcal{F}_R$ on θ_u and f are shown in Figure 6. For all f of interest, $\mathcal{F}_R(\theta) = \mathcal{F}_R(0)\cos^{2m}\theta$, to high precision, particularly for $|\cos\theta| \geq 0.3$. The values of m obtained by least-squares fitting over this range are likewise shown in this figure. Interestingly, m is itself very well fit by a simple empirical function, $m = 1 - {}^1/_2\exp(-2/\sqrt{f})$, which correctly exhibits the limits of 1 and ${}^1/_2$, respectively, as f tends to zero and infinity.

The static field is obtained much more simply. Under the assumption that the solvent adopts the lowest energy orientation, it may readily be shown[29]

$$\mathcal{F}_S = (2\mu_v/R^3)[\tfrac{1}{2}(1 + 3\cos^2\theta_u)^{1/2}] \tag{A15}$$

Other than the lowest energy orientations could result in a different angular dependence, but not, if fixed, in any other functionality change.

The overall field produced along the solute dipole axis by a second or more equidistant solvent molecule(s) will therefore be

$$\mathcal{F}_v = \mathcal{F}(0)g(\theta_u) \tag{A16}$$

$$\begin{aligned} g_R(\theta) &= \textstyle\sum n_i\cos^{2m}\theta_i \\ \mathcal{F}_R(0) &= (kT/\mu_u)(2f\coth 2f - 1) \\ g_S(\theta) &= \tfrac{1}{2}\textstyle\sum n_i\sqrt{1 + 3\cos^2\theta_i} \\ \mathcal{F}_S(0) &= (kT/\mu_u)(2f) \end{aligned} \tag{A17}$$

where g can be substantially larger than unity upon multiple solvation on the spherical locus. Nevertheless, proportionality with the effect of a single on-axis solvent can be anticipated. In the event the solute dipole is not located at the center of a spherical cavity as the foregoing constant-R analysis and for that matter all continuum models of present concern imply, equally and even more profound reaction field effects may be noticed upon multiple solvation. Some may be incorporated by factors within f (cf. ref 4c); others may require explicit recognition of changes in R as well as θ. This shall not be pursued further here for any mode, specific interaction or continuum, however.