J. Am. Chem. Soc. 1982, 104, 4793–4798

Solvent Dielectric Attenuation of Substituent Effects. Field Transmission Dependence on Cavity Boundary Representation[1]

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Abstract: Previously developed methods for introducing radial dependence to the bulk dielectric of continuum solvents in order to take into account electrostatic field effects at and near the cavity boundary have been applied to the Kirkwood–Westheimer (KW) substituent–reactivity theory. Functions assumed to model electrical saturation and electrostriction are shown capable of causing from 10% to fourfold variations in typical solvent effects on pole–pole and pole–dipole interactions within spherical cavities. The relative effects on the latter are significantly larger; their introduction generally improves the agreement of theory with reactivity observables. Various intrinsic details of the original and modified theories are examined by means of generalized geometry dependencies for $\epsilon_{\rm eff}$ and the possible interrelation of site location and dielectric modification effects scrutinized. Extensions to cavities of other shapes and to anisotropies for the bulk dielectric are also briefly outlined.

Perhaps the most serious conceptual problem inherent in modelling solvent as a continuous dielectric concerns the nature of the boundary region where the solute is presumed to end and the solvent continuum to begin. Shape is only part of this problem and, unless severely irregular, likely not the most important part.[2] Molecular ordering effects on the dielectric constant across the boundary due to electrostatic saturation and/or electrostriction were recognized as possible complications around the same time the space-filling nature of the solute within the continuum was realized.[3] Nevertheless, in the intervening 40 years, with the exception of attempts to account for specific molecular associations in dipole moment theory,[6] little has been done to sort out and evaluate the importance of these classical electrical effects, despite the remarkably broad interest the theories continue to arouse and persistent reminders of their deficiencies.[7]

Recent efforts to remove the physically unrealistic discontinuous change of the local permittivity at the cavity boundary, consistent with the above-mentioned electrical effects, have produced some notable improvement in Onsager dipole moment theory results. Of no less interest are their implications for substituent-reactivity theory. Block and Walker,[11] proposing an inverse exponential radial dependence for the permittivity, mainly because analytical solutions of the Laplace equation are possible with it, found the resultant fields capable of substantially improving liquid- to gas-phase dipole moment correlations for a variety of nonassociating molecules. More recently, means to completely remove the differential equation solvability constraints, and thereby allow more realistic spatial permittivity dependencies, have been developed and similarly employed.[12] Because of the general nature of the modification method, it seemed plausible that related analytic and numerical techniques could provide solutions to the electrostatic work equations for spatially inhomogeneous media upon which evaluation of attenuated substituent field effects depend.

The present report contains details of such studies on cavities of spherical shape, both for polar and dipolar substituents interacting with polar probe sites. Permittivity functions previously used in the dipole moment studies are reexamined in the present, often stronger field context, and others to which greater physical significance may attach, particularly as regards the described near-boundary effects, are likewise introduced and contrasted. The results of these studies appear to provide strong support for the view that neglect of such cavity edge effects are principal deficiencies of KW theory. Moreover, they are capable, in concert with more realistic (nonaveraged) location strategies for the interacting sites, of rationalizing the important historical observation[9,10,13] that solvent attenuation of dipolar substituent effects tends to be much more seriously overestimated than that of polar effects within continuum theories. Finally, relevance of the present methods to possible improvements of ellipsoidal cavity models and how these may be made to eventually mimic some specific as well as bulk solvation effects are also briefly examined.

Theory, Model Modifications, and Numerical Methods

Space may be divided and potentials specified for present purposes in much the same way as in the Onsager theory modifications,[12] with the one important qualification of noncentrosymmetric charge distribution within the cavity. Therefore, adopting the Kirkwood notation[5a] except for ϵ rather than D as dielectric constant, eq 1 is obtained, where Ψ_{sj} is the potential for

$$\Psi_{in} = \sum_{k=1}^{t\ \text{charges}} \frac{e_k}{\epsilon_i |r - r_k|} + \sum_{n=0}^{\infty} \sum_{m=-n}^{n} B_{nm} r^n P_n{}^m(\cos\theta) e^{im\phi}$$

$$\Psi_{sj} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \left\{ \frac{C_{jnm}}{r^{n+1}} + G_{jnm} r^n \right\} P_n{}^m(\cos\theta) e^{im\phi}$$

$$\Psi_{ex} = \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{A_{nm}}{r^{n+1}} P_n{}^m(\cos\theta) e^{im\phi} \qquad (1)$$

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(1) 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.

(2) Recent publications in the same or related veins to the present from which additional literature references may be obtained are: (a) S. Ehrenson, *J. Am. Chem. Soc.*, **98**, 7510 (1976); (b) *J. Phys. Chem.*, **81**, 1520 (1977); (c) *Chem. Phys. Lett.*, **56**, 523 (1978). Others also recent bearing on this question are: (d) W. H. Orttung, *J. Am. Chem. Soc.*, **100**, 4369 (1978); (e) Z. Friedl, J. Hapala, and O. Exner, *Collect. Czech. Chem. Commun.*, **44**, 2928 (1979).

(3) Onsager's[4] improvement of the Debye theory of dipole moments and Kirkwood and Westheimer's (henceforth KW)[5] of the Bjerrum–Eucken substituent reactivity theory by explicit introduction of the "solute" cavity are individually familiar, but often not connected.

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

(5) (a) J. G. Kirkwood, *J. Chem. Phys.*, **2**, 351 (1934); (b) J. G. Kirkwood and F. H. Westheimer, *ibid.*, **6**, 506 (1938); (c) *ibid.*, **7**, 473 (1939); (d) F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(6) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939); H. Frohlich, "Theory of Dielectrics", 2nd ed, Oxford University Press, London, 1958.

(7) Mainly, in the present context of KW reactivity theory, when rigid molecular framework systems allow better definition of cavity shapes and separation distances between interacting sites than is usually possible. See, e.g., Westheimer's comments on the Roberts and Moreland bicyclooctane results[8] (ref 24 there) and other rigid system results analyses.[9,10]

(8) J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(9) G. W. Wheland, "Advanced Organic Chemistry", 3rd ed, Wiley, New York, 1960, Chapter 11.

(10) H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **86**, 5188 (1964).

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

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

(13) C. Tanford, *J. Am. Chem. Soc.*, **79**, 5348 (1957).

points lying within the spherical shell, j. The medium outside cavity is divided among such shells nested contiguously and concentrically, the dielectric constant of each of which is $\epsilon(r_j)$, where r_j is some convenient function of the inner and outer dimensions of the shell and

$$\epsilon_i < \epsilon(r_1) < \cdots < \epsilon(r_j) < \epsilon(r_{j+1}) < \cdots < \epsilon_{ex} \lesssim \epsilon_B \; (=\epsilon_{bulk}) \tag{2}$$

By this means, in the limit of increasing number of shells of decreasing thickness can the radial inhomogenity of the medium be conveniently incorporated. Further details by which eq 1 are solved through imposition of the appropriate boundary conditions are to be found in the Appendix and ref 12. What is ultimately sought is B_n, the present model equivalent of the linear Ψ_{in} coefficient of Onsager (dipole moment) theory which directly yields the reaction and/or cavity fields of that theory. Here B_n provides solution of the KW electrostatic work equation (viz., eq 6 of ref 5b)

$$W = \frac{1}{2}\sum_{k,l=1}^{t}\frac{e_k e_l}{\epsilon_i r_{kl}} + \frac{1}{2}\sum_{n=0}^{\infty} B_n \gamma_n \tag{3}$$

where

$$\gamma_n = \sum_{k,l=1}^{t} e_k e_l r_k{}^n r_l{}^n P_n(\cos\theta) \tag{4}$$

which, as in the homogeneous medium model, depends only on the charge distribution *within* the cavity.

In fact, the entire development, including limitations such as neglect of self-energy terms for the charge distributions and questions as to energy and entropy separation, is now identical with that of KW theory, leading for the development of two charges (1, 2), e.g., as in successive ionizations of diabasic acids, to

$$\Delta W = kT \ln \{\sigma_{\mathrm{symNo}}(K_1/K_2)\} = e^2/(r_{12}\epsilon_{\mathrm{eff}}) \tag{5}$$

and hence,

$$\epsilon_i/\epsilon_{\mathrm{eff}} = 1 + (r_{12}/b)\sum_{n=0}^{\infty}(n+1)x^n F_{n,1} P_n(\cos\theta) \tag{6}$$

The parameters x ($= r_1 r_2/b^2$, where r_1 and r_2 are the distances from cavity center to the developed charges), r_{12} (the intercharge distance), and θ (the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$) retain their original meanings, although extended to include nonidentical interacting site locations, i.e., r_1 not necessarily equal to r_2.

In very similar ways, and by employing the point-dipole-limit method of ref 5b (particularly sect IV), the equivalent and likewise generalized pole–dipole expression can be obtained:

$$\epsilon_i/\epsilon_{\mathrm{eff}} = 1 + (r_{12}{}^2/r_2 b \cos\alpha)\sum_{n=0}^{\infty}(n+1)x^n F_{n,1} \times \{(n+1)(\sin\phi)V_n + n(\cos\phi)W_n\} \tag{7}$$

Here, ϕ and α are the angles made by the projection of the dipole into the plane containing its center (point 2), the pole (point 1), and the origin of the sphere with respectively the vectors r_2 and r_{12} (see Figure 1). W_n and V_n are respectively P_n (the Legendre polynomial with its argument, $\cos\theta$, here and henceforth suppressed) and $(\cos\theta\, P_n - P_{n+1})/\sin\theta$.

The $F_{n,1}$ coefficients are evaluated in much the same way as were the cavity and reaction field coefficients in ref 12. In fact, as implied above and in the Appendix, $F_{1,1}$ is equal to half the reaction field parameter, t, and, moreover, all $F_{n,1}$ correctly reduce in the limits of equal shell permittivity and vanishing radius (for finite η) to the unmodified KW theory result

$$F^0{}_{n,1} = \frac{(\epsilon_B - \epsilon_i)}{[(n+1)\epsilon_B + n\epsilon_i]} = \frac{1-\omega}{n+1+n\omega} \tag{8}$$

Technical details concerning generation and storage of the modified model $F_{n,1}$, prior to their use in eq 6 and 7, are also to be found in the Appendix.

Attention is now directed to the radial permittivity functions, specifically as regards their capacity to model dielectric inhomogeneities near the cavity boundaries. Previous results obtained in the dipole moment theory studies,[12] and subsequent applications to correlation of solvent (di-) polarity scales,[14] suggest the inverse exponential dependence used by Block and Walker overcorrects the original (Onsager step-function) variation of the dielectric constant at the boundary. A direct exponential function, which assumes the mean of the boundary and bulk values is reached at the outer edge of the first solvation shell, also appears, on the basis of such correlations, to overcorrect the rate of change of $\epsilon(r)$.

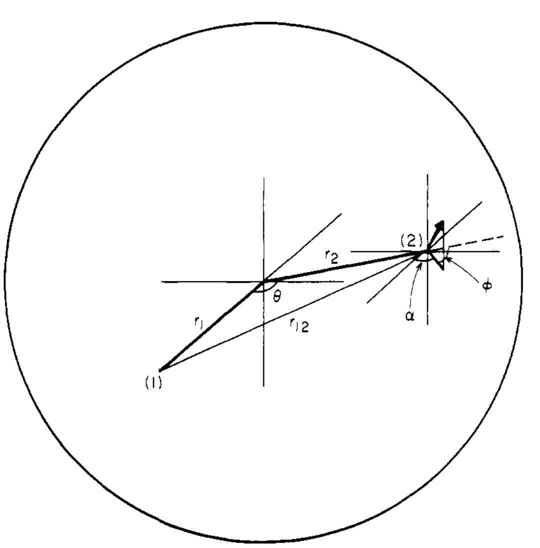

Figure 1. Interacting pole (1)–dipole (2) pair within spherical cavity of radius b.

On the other hand, an inverse fourth-power function derived from expansion of the external field dependence of $\epsilon^{12,15}$ seems from these correlations to underestimate the needed correction. This function, which should realistically reflect electrical saturation caused by a centrally located pole (ion) at and near the interface of its nonconducting spherical envelope, may, however, have been inappropriate in the correlated systems for several reasons, not the least important of which concerns the weak (dipolar) and directional nature of the molecular interactions there. In the present studies, where the probed phenomenon generally involves formation (or neutralization) of an ionic site, albeit at a noncentral cavity location, an inverse fourth- (or therebout)[16] power function may be more appropriate.

Electrostriction of the medium near the cavity edge is the other classical refinement of continuum solvent models of interest. Depending upon whether the nature of the near-cavity region is viewed as relatively diffuse, or dense and incompressible, would determine the functional electrostrictive dependence of $\epsilon(r)$, specifically through changes in the effective local density. The diffuse condition would result from the presence of a few solvent molecules whose positions were effectively averaged around the cavity, itself considered as vacuum containing the single solute molecule. While perhaps satisfactory in this region, this view of the medium cannot well represent the solvent further away, where more representative bulk liquid properties are expected. Nevertheless, constructing a continuous dielectric function to cross the cavity interface is much more easily accomplished and physically rationalized assuming a diffuse solvent region immediately outside.

Consequently, both extremes are examined under the assumption that the local density at any distance r from the center

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(14) S. Ehrenson, *J. Am. Chem. Soc.*, **103**, 6036 (1981).

(15) A. D. Buckingham, *J. Chem. Phys.*, **25**, 428 (1956); *Discuss Faraday Soc.*, **24**, 151 (1957).

(16) Off-center site location here may, within limits, be accommodated by slightly modified $\epsilon(r)$ dependence in ways similar to eccentric dipole contributions to the reaction field in dipole moment theory.[17]

(17) C. J. F. Bottcher, "Theory of Electric Polarization", Vol. 1, 2nd ed, revised by O. C. Van Belle, P. Bordewijk, and A. Rip, Elsevier, Amsterdam, 1973, Chapter IV.

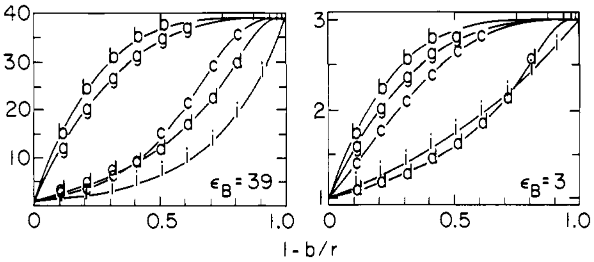

Figure 2. Variation of ϵ with $1 - b/r$ for ϵ_B of 39 and 3. The labels b and g are for the inverse fourth- and third-power functions, respectively, c for Clausius–Mossetti function, and d and i for the direct and inverse exponential functions. Tics across the tops of the figures indicate successive increases of r by a factor of 2.

of the cavity is proportional to the volume of the solvent shell this radius implies, divided by the entire spherical volume of the same radius, i.e., shell plus cavity. The diffuse and dense medium radial functions are then respectively

$$\epsilon = 1 + \alpha(1 - (b/r)^3) \qquad \text{diffuse medium}$$

$$\epsilon = \frac{1 + 2\beta(1 - (b/r)^3)}{1 - \beta(1 - (b/r)^3)} \qquad \text{dense medium}$$

where α is $\epsilon_B - 1$, $\beta = \alpha/(\epsilon_B + 2)$ and here and henceforth all ϵ are expressed relative to ϵ_i. The former function, it will be immediately recognized, arises from the porportional relation of the dielectric constant to the density through the susceptibility and the latter from the Clausius–Mossetti equation.[18,19]

Included for convenient reference as well are explicit statements of the other functions discussed and examined:

$$\epsilon = \epsilon_B \qquad \text{unmodified (Onsager)}$$

$$\epsilon = 1 + \alpha(1 - (b/r)^4) \qquad \text{pole (ion) saturation}$$

$$\epsilon = \epsilon_B - \alpha 2^{-(r-b)/|(n-1)b|} \qquad \text{direct exp. satn}$$

$$\epsilon = {\epsilon_B}^{1-b/r} \qquad \text{inverse exp. satn}$$

The parameter n of the direct exponential function indicates where (i.e., at how many cavity radii) the mean of the boundary and bulk dielectric is reached. As previously discussed and used, n equals 3.

Figure 2 shows the variation in ϵ, for representative large and small ϵ_B, with change in r, actually $1 - b/r$, for these functions. Several points are noteworthy, particularly those influencing the latitude of the study. For both large and small ϵ_B, the inverse power functions very rapidly, and the inverse exponential functions rather slowly approach their bulk dielectric limits with increasing r, in harmony with previous understanding. The dense medium function, in contrast, shows considerable difference in this variation for large compared to small ϵ_B, being reasonably well approximated by the direct exponential function when ϵ_B is large, but where ϵ_B is small, behaving, as expected, much as the diffuse medium function (which is its limit as $\epsilon_B \to 1$). As a result, there seems little need to explicitly consider the dense medium function; on the same grounds of strong overlap, any conclusions sought for the inverse power function should be extractable from the diffuse (inverse third-power) function results.

Results and Discussion

Solvent Modification Effects as Functions of Molecular Size and Shape. Figure 3 shows typical variations of the effective dielectric constant with changes in x forthcoming from the original (KW) and the two modifications of present interest. In all cases, here and henceforth the upper curve is for the pole–pole interaction and the lower for the pole–dipole interaction cases. These curves, taken individually, all resemble those presented in the original work;[5b] taken together, however, they reveal the profound effects physically realistic bulk permittivity modification can have on ϵ_{eff}. Whereas the inverse power function modification (G) results in 10–15% smaller values for the pole–pole (p–p) interaction cases, the more radical direct exponential function modification (DE) decreases ϵ_{eff} by more than a factor of 2 for poles located near the spherical cavity surface.[20] The effects on the pole–dipole (p–d) interaction cases are much greater, being as large as a factor of 2 for the G and 4 for the DE modification in the high x ($\sim$ 0.9) region, especially for large ϵ_B. This result has obvious implications to the relatively poorer predictions of dipolar compared to polar substituent attenuation effects obtained from original theory applications.

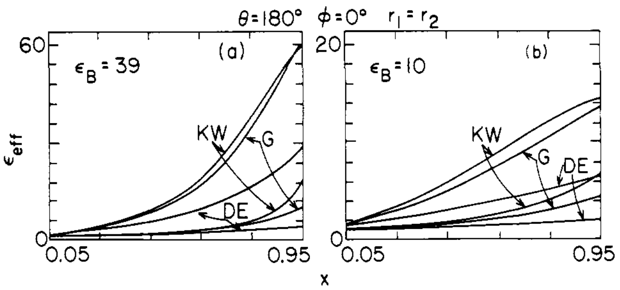

Figure 3. Variation of ϵ_{eff} with x for interacting sites on sphere diameter in solvents of (moderately) high and low bulk dielectric constant.

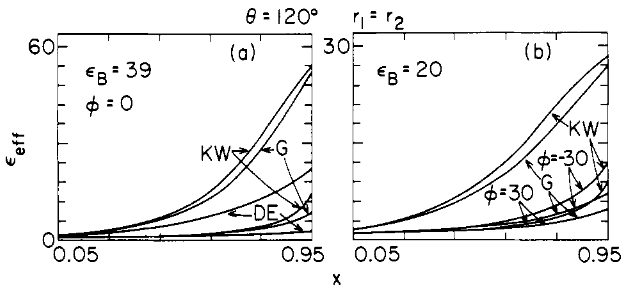

Figure 4. Variation of ϵ_{eff} with x for off-diameter interacting sites.

Figure 4 shows similar variations for cases where the interacting sites do not lie on a diameter. Few differences beyond the disappearance of the high-x p–p curve crossing anomaly are to be seen upon comparison with Figures 3a and 4a. Careful analysis reveals the attenuation effects to be very slightly greater here than in the θ = 180° conformation. In Figure 4b, the effects of orientation of the dipole vector are indicated both in the original and inverse power function modified theories. The orientation, ϕ = −30°, it should be recognized, corresponds to the dipole vector colinear with the vector r_{12} (i.e., cos α = 1) and the other, ϕ = 30°, substantially displaced from colinearity. Apparently, such orientation effects, as with others already observed and several following, only become significant as the interacting sites approach the cavity boundary ($x \to 1$). Note as well, as before, significant differences in ϵ_B only produce differences in degree, not kind, in these ϵ_{eff} plots.

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(18) Cf. M. Abraham and R. Becker, "The Classical Theory of Electricity and Magnetism", 2nd ed., Blackie and Son, Ltd., London, 1950, Chapter V.

(19) C. K. Ingold, *J. Chem. Soc.*, 2179 (1931), early attempted to evaluate electrostrictive effects on incompressible solvent permittivities via the Clausius–Mossotti equation, unfortunately without recognizing the possibilities of moderation of such effects by the solute-containing cavity.

(20) For large ϵ_B, in the limit of increasing x, it appears that the inverse power function (G) ϵ_{eff} values may slightly exceed the unmodified function values (see Figure 3a), although this may well be an artifact of rounding for the large number of terms necessary for convergence of the respective sums. On the other hand, the analytic and summed KW values differ little (e.g., for x = 0.95, ϵ_B = 39, they are respectively 59.60 and 59.45, whereas the G-function value is 61.40). While judgment should at present be reserved, near-boundary refractions may yet be found to produce other surprises than $\epsilon_{\text{eff}} > \epsilon_B$ and nonmonotonicity of ellipsoidal cavity ϵ_{eff} functions noted in earlier studies,[2a] particularly for extreme but not necessarily only unrealizable configurations. See also ref 2b and compare with Figure 4 here and with the closely related results and major conclusions of ref 2d, especially as regards sensitivity to the dielectric constant specified at the solute–solvent interface. The finite element method employed there, it should further be noted, is a likely alternative to the presently described method for investigation of inhomogeneous medium systems.

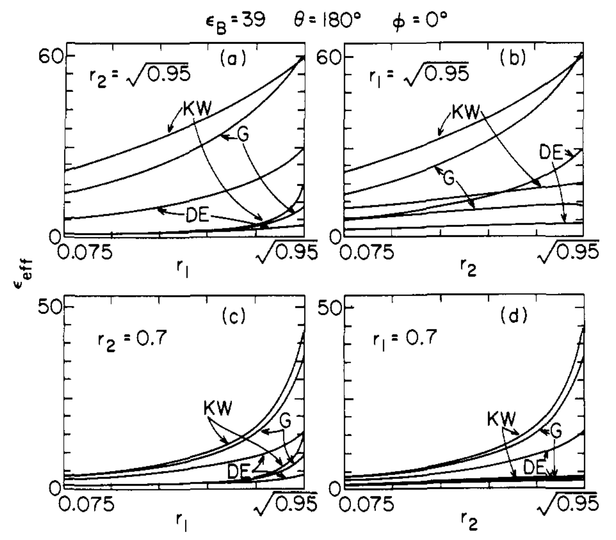

Figure 5. Variation of ϵ_{eff} with r_1 and r_2, the other length being held corresponding to location near and substantially in from the cavity boundary.

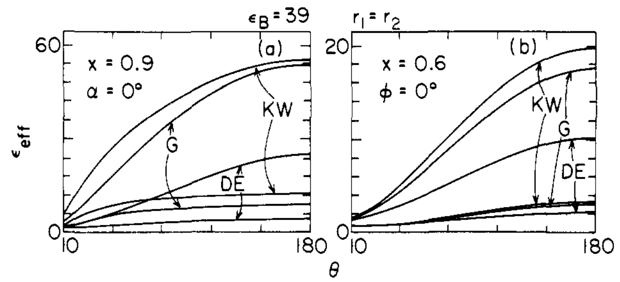

Figure 6. Variation of ϵ_{eff} with the central angle θ for cases where the interacting site locations and dipole orientation are significantly changed.

Table I. Permittivity Modification Effects on ϵ_{eff}[a,b]

constant r	mod	p-p	p-d r_1 var	p-d r_2 var
$\sqrt{0.95}$	G	1.03-0.70	0.58-0.98	0.64-0.60
	DE	0.48-0.29	0.23-0.92	0.23-0.26
0.7	G	0.83-0.93	0.63-0.98	0.92-0.94
	DE	0.36-0.72	0.25-0.93	0.70-0.82
x var	G	1.03-0.89	0.58-1.	
$(r_1 = r_2)$	DE	0.44-0.80	0.23-1.	

[a] $\epsilon_{eff}(\text{mod})/\epsilon_{eff}(\text{KW})$ ranges for physically accessible high to low values of the variable r's ($\sqrt{0.95}$-0.25) with $\epsilon_B = 39$.

[b] Remarkably little difference is noted for these ratios upon significant change in ϵ_B; e.g., reduction of ϵ_B by a factor of 2 causes less than 0.05 change in all entries with the exception of the DE(p-p) low x value which becomes 0.89. Increase in ϵ_B by a factor of 2 causes changes greater than 0.05 only for the high r_1, r_2, and x p-d interaction values in the $\sqrt{0.95}$ row to 0.76 for G and to 0.30 for DE. For the latter, the corresponding low parameter range values are also shifted up, but by less than 0.1 except for the x p-p interaction entry which becomes 0.94.

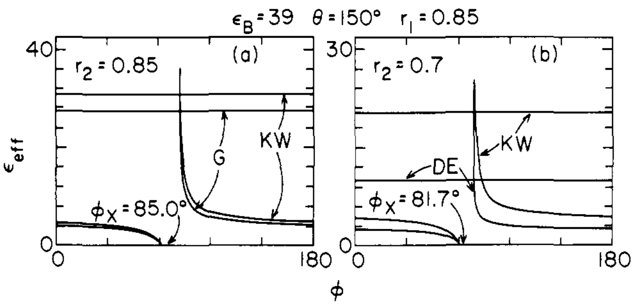

Figure 7. Variation of ϵ_{eff} with the dipole orientation angle ϕ for two site location conditions and permittivity modifications. Note ϕ_x signifies the crossover (discontinuity) for the KW function; both the G function in (a) and the DE function in (b) discontinuities occur at slightly smaller ϕ.

It is appropriate at this point to recognize the historical constraint of equality of the **r** vector lengths as physically unrealistic, particularly for the dipole substituent cases. This was originally adopted as a simplifying expedient in theory development where major attention was directed to successive ionization processes, i.e., where polar substituent effects pertain. Figure 5 gives some indication of the importance of location of the interacting sites on the basis of their individual natures and the depths of possible pitfalls accompanying casual simplifications.

The first feature to be noted, in contrast to earlier behavior, is the maintainance of sizable ϵ_{eff} values in the limits of decreasing varied r (particularly, p-p values in Figure 5a, and both p-p and p-d in 5b). Upon reflection, this appears generally reasonable in that, even in the limit, substantial distances separate the interacting sites, one of which lies near the cavity boundary. The limiting ϵ_{eff} values in Figures 5c and 5d are correspondingly smaller, reflecting the greater imbedding of the invariant site there. Perhaps more suprising is the observation (in Figure 5a and somewhat less obviously in 5c, compared to Figure 3) that the p-p interactions are considerably more strongly affected by whether the positions of the other site is moved. This is borne out strikingly by the 5b and 5d plots, where essentially constant ϵ_{eff} is seen to persist over wide r_2 length variation.

Also obtainable from these figures with a bit more effort is the fact that substantially greater effects on ϵ_{eff} may accrue through permittivity modification when one site is located near the cavity edge and the other is not. The p-p effects range up to ~30% upon G-function modification to almost a factor of 4 upon DE function modification. The p-d effects, on the other hand, are not significantly greater than the largest previously observed (e.g., at the high-x range in Figure 3) and do not vary much with variation in r_2. Deeper imbedding of the position-invariant site is found to have substantial effects on the r_2 variation plots, but little for the r_1 plots. These results are summarized in Table I; their implications, particularly as regards predicted attenuation of dipolar substituent effects, are most striking.[21]

Typical variation of ϵ_{eff} with θ is shown in Figure 6. In Figure 6a, for sites close to the boundary and dipole vector pointed directly toward (or away from) the polar site, whereas the p-p interaction is observed to fall off roughly proportionally to cos θ, the p-d interaction is essentially invariant down to small θ. In Figure 6b, where $\phi = 0$, i.e., where the dipole vector points directly toward the sphere center, ϵ_{eff} decreases similarly for the p-d and p-p interactions.

As a final illustration of how ϵ_{eff} depends upon size and shape of the encapsulated molecule and perhaps more graphically indicative of what ϵ_{eff} really implies, consider the plots in Figure 7. The independent variable here is ϕ, the angle made by the dipole projection and r_2 vectors; in each case r_1 and θ are 0.85 and 150°, respectively. The straight lines are for the p-p interactions, which of course are invariant to changes in ϕ but serve to clearly reiterate the 10-15% reduction by G and a factor of

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(21) An illustration of the possible distortions caused by site averaging is to be found in the oft-examined ΔpK_a values for 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids. Tanford[13] reasonably increased the imbedding distance for dipolar substituents to 1.5 Å (from either 1 Å or that dictated by the Traube volume) and found that this change would substantially improve agreement with the experimental values (e.g., as measured by Roberts and Moreland[8] and previously computed from a Traube sphere or ellipsoid). In fact, the improvement is almost solely due to the recognizably questionable procedure of using the average r-length approximation (i.e., the $r_1 = r_2$ form of eq 7); for the 4-Br substituted case, for example, rather than ϵ_{eff} decreasing by ~40% from the Traube volume value, less than a 15% decrease is computed when the individual r_1 and r_2 are used. (Moreover, if the midpoint of the molecular length is not used to define the sphere center, the decrease is even less, amounting to only 5% rather than 30%.) These results, in harmony with the above observation that r_2 variation is only weakly reflected in ϵ_{eff} bear importantly on the question of imbedding distances for polar sites (crucial) vs. dipolar sites (of secondary concern) and how modifications of the dielectric function may rationally contribute to an improved continuum solvent theory.

2 by DE modification of ϵ_{eff} for typical p–p interactions.

The ϵ_{eff} plots for the p–d interactions are novel and much more interesting, slowly varying in the region where the dipole and r_{12} vectors are colinear, to regions of large ϵ_{eff}, and eventually to infinite discontinuities for the KW curves at ~85 and 82°, respectively, in Figure 7a where $r_2 = r_1$ and Figure 7b where $r_2 < r_1$. While superficially troubling as regards questions of physical significance, examination of the derivation of eq 2–7 provides a ready explanation. The discontinuities arise solely because of the definition of ϵ_{eff} in terms of ΔW, relative to that in homogeneous space, in the absence of cavity. What is implied by the discontinuity is that ΔW for this configuration is zero, in the specified cavity; i.e., cancellation of the pole interactions with the + and − ends of the dipole occurs and hence no finite value of ϵ_{eff} can reproduce the interaction for this configuration in free space.

This may be more easily grasped when the angle α, as shown in Figure 1, for the crossing of the dipole projection and r_{12} vectors is considered. In Figure 7a, α is 80.0° and in 7b it is 81.8° for the KW functions and slightly closer in each case to $\pi/2$ for the modified functions. It is the difference from $\pi/2$, it should be recognized, that is significant since, in the limit of disappearance of cavity or upon approach of ϵ_{bulk} to ϵ_i, the discontinuity would occur where the dipole vector is normal to r_{12}.[22]

What this implies physically is that encapsulated interacting sites in media of substantially different electrical transmission properties may only be representable in free (i.e., homogeneous, unbounded) space terms upon drastic changes in the free space properties such as permittivity or, perhaps, in some extreme situations, not at all. Every such apparent anomaly, it is here suggested, including those of footnote 20 and numerous others of historical note, arise solely or mainly because reference to an equivalent free space system is demanded.

Prediction and Rationalization of Solvent-Moderated Substituent Effects. Compared to the original cavity model results, such quantities as the $\Delta \text{p}K_\text{a}$s for symmetric dibasic acids should be from 10% to a factor of 2 larger, through reduction of ϵ_{eff}, depending upon the relative importance of the proposed saturation and electrostriction modifications, and upon the size of the molecule. Effects in the low range, as would follow G-function imposition, appear most compatible with the observed acidities,[23a,24] favoring in general presumption of greater extension of nonrigid frameworks than the original theory, which seems plausible. The sizes of the resultant corrections viewed against the relative successes of the original theory, which is recognizably incomplete at many levels, suggests only limited claims of efficacy for the modifications are supportable by these diacid data, however. Essentially the same results and conclusions are forthcoming from examination of some unsymmetric diacids,[23b,24] where meaningful comparisons are even more limited in scope.[25]

It is in the rationalization of solvent influence on dipolar substituent effects that the permittivity modification effects appear to become truly significant. Factors of 2 to 4 (decrease in ϵ_{eff}, increase in $\log K/K_\text{H}$) have been shown to routinely occur upon imposition respectively of the G and DE functions (Figures 3 and 5, and Table I). These should be recognized as on the order of the size correction generally needed to bring KW theory results into reasonable agreement with observation,[8–10,28] without resort to radical changes in the dipole imbedding factors (which, in fact, may not be as efficacious as earlier believed[21]). Here, in contrast to the diacid comparison, either or both saturation and electrostriction effects appear plausible, although in the extreme (of large x) and in combination with G, the DE function appears likely to overcompensate for the original theory deficiencies.[29]

Contrasts with the corrections sought by interacting site relocation (i.e., change in the imbedding distances) and, ultimately, how these changes and the permittivity modifications interrelate are matters deserving of some attention. Moving the interacting site(s) further into the sphere generally results in a decreased ϵ_{eff} (although this may or may not occur as rapidly as earlier believed; see Figure 5 and discussion thereof), a change which parallels the effects of permittivity modification. At the same time, the latter, largely because of their continuity properties at the cavity boundary, are recognized to generally mitigate the physical changes modeled there and as a result render more flexible any assumption of where the solute ends and solvent begins. How these changes may be quantitatively combined in physically reasonable models for solvation is, however, best deferred until such other questions of cavity shape and permittivity anisotropy effects are examined, as they will be in forthcoming studies.

It should be noted that the same techniques for modification of the solvent continuum developed for spherical cavities should be directly transferable to cavities of other shapes. Furthermore, whereas present interest was restricted to spherical solvent shells, there is no reason why generalization to other shapes for these shells should not also directly follow. Various assumptions concerning changes in medium permittivity as functions of distance from the interacting sites could well require models of spherical or ellipsoidal cavities nested within other ellipsoids of varying shapes (e.g., eccentricities, foci location). The numerical problems may be more complicated; there seems no reason at present to believe the field theory from whence the ϵ_{eff} equations arise would be.

Appendix

Derivation of the B_{nm} Relations. Following Neumann expansion of the first term of ψ_{in} (see e.g., ref 5a), imposition of the dielectric and dielectric displacement equality constraints at the $\eta + 1$ boundaries of space (for η contiguous shells) provides $2(\eta + 1)$ equations to evaluate an equal number of eq 1 coefficients (viz., one each B and A plus η each C and G) for *each spherical harmonic term, nm*. At this point, the major difference from the Onsager theory modification may be delineated; because of centrosymmetric dipole location in the latter only the $n = 1$ term applies. Nevertheless, the difference is recognizable as one of degree and not of kind, leading to a *series* of equations in the present case running over the index n which are analytic in this index. Each set, for given n, is in turn solvable by the same kind of downward recurrence as employed in the dipole theory procedure.

Specifically, the coefficients A_n (index m drops through the spherical harmonic addition theorem) are removed upon simultaneous solution of the dielectric constraint equations at the outer shell boundary ($r = \rho_\eta$), leaving $C_{n\eta}$ as a function of $G_{n\eta}$. This is followed by solution of $C_{n,\eta-1}$ as a function of $G_{n,\eta-1}$ from the pair of equations relating to the next inner boundary upon removal of $C_{n,\eta}$. In such a manner, relation of the conjugate pairs C and

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(22) Another, complementary, discontinuity is also encountered when α is exactly $\pi/2$, see, e.g., eq 7. This corresponds to a null-work configuration for the free-space interaction, and as such cannot reproduce the in-cavity energetics through any ϵ_{eff} value.

(23) See, e.g., F. H. Westheimer and M. W. Shookhoff, *J. Am. Chem. Soc.*, **61**, 555 (1939): (a) Table I; (b) Table II, but subject to the usual cautions about where spherical cavities may be appropriate.

(24) J. T. Edward, P. G. Farrell, and J. L. Job, *J. Chem. Phys.*, **57**, 5251 (1972), especially Table V.

(25) Acidities of short-chain α,ω-amino acids, when alternatively examined in the context of monopolar substituent effects ($\Delta \text{p}K_\text{a}$, with references to unsubstituted acids) are grossly exaggerated by the original theory[26] and, if anything, even less satisfactorily modeled when the present modifications are introduced. A number of likely reasons for this failure may be cited, principal among which are the impropriety of comparing different order terms of the multipole expansion and associated interacting site location uncertainties, particularly with the expectation that the necessary cancellations would occur in ΔW to maintain viability of the model. Similar problems may also be involved in the apparent shortcomings of effective dielectric theory to correlate solvent attenuation of charged substituent effects on $\text{p}K_\text{a}$ values of more rigid acids observed by Wepster.[27]

(26) J. Kirchnerova, P. G. Farrell, J. T. Edward, J.-C. Halle, and R. Schaal, *Can. J. Chem.*, **56**, 1130 (1978); J. T. Edward, P. G. Farrell, J.-C. Halle, J. Kirchnerova, R. Schaal, and F. Terrier, *J. Org. Chem.*, **44**, 615 (1979).

(27) A. J. Hoefnagel, M. A. Hoefnagel, and B. M. Wepster, *J. Org. Chem.* **43**, 4720 (1978); A. J. Hoefnagel and B. M. Wepster, *ibid.*, in press.

(28) F. W. Baker, R. C. Parrish, and L. M. Stock, *J. Am. Chem. Soc.*, **89**, 5677 (1967).

(29) In other applications as sole modification of Onsager solvent behavior,[12] or in combination,[14] the DE function as parametrized appears almost as exaggerated as the Block and Walker[11] function.

G to each other, inward through the medium to the solute cavity boundary finally allows solutions of the B_n coefficients in terms of the Neumann harmonics for the intracavity charge distribution.

In practice, the following recurrence equations are developed

$$F_{n,\eta+2-j} = \frac{\epsilon_{\eta+2-j}(1 + nL_{j-1}) - \epsilon_{\eta+1-j}(1 - (n + 1)L_{j-1})}{(n + 1)\epsilon_{\eta+2-j}(1+nL_{j-1}) + n\epsilon_{\eta+1-j}(1 - (n + 1)L_{j-1})} \qquad \text{(A1)}$$

and

$$L_{j-1} = R^{2n+1}_{\eta-(j-1)} F_{n,\eta+2-(j-1)} \qquad \text{(A2)}$$

where $R_{\eta-j} = (\rho_{\eta-j}/\rho_{\eta-(j-1)})$, $F_{n,n+2} = L_0 = 0$ and, consequently, $F_{n,\eta+1} = F_{\mathrm{n,ex}} = [\epsilon_{\mathrm{ex}} - \epsilon_\eta]/[(n + 1)\epsilon_{\mathrm{ex}} + n\epsilon_\eta]$. Therefore,

$$B_{nm} = \frac{-(n + 1)[\epsilon_1(1 + nL_\eta) - \epsilon_i(1 - (n +1)L_\eta)]E_{nm}}{b^{2n+1}\epsilon_i[(n + 1)\epsilon_1(1 + nL_\eta) + n\epsilon_i(1 - (n + 1)L_\eta)]} \qquad \text{(A3)}$$

$$B_{nm} = -(n + 1)F_{n,1}b^{-(2n+1)}E_{nm}/\epsilon_i \qquad \text{(A4)}$$

where E_{nm} is the Neumann harmonic term for the t (in number) poles

$$E_{nm} = [(n - |m|)!/(n + |m|)!]\sum_{k=1}^{t} e_k r_k^n P_n^m(\cos \theta_k)e^{-im\phi_k} \qquad \text{(A5)}$$

and b is the radius of the cavity.

Generation and Testing Procedures for the $F_{n,1}$ Coefficients. The double limit procedure and damped geometric mean extrapolation technique of ref 12 are maintained with convergence threshold decreased to 10^{-5} to reduce significant figure losses upon extended summation in eq 6 and 7. The outer radius function for a given shell, the ith, upon which the dielectric constant was assumed to depend, was generally parametrized as previously outlined through the function, $b[(\eta + f)/i]^p$, with between 512 and 2048 shells, most often 1024, required for convergence. As well, in harmony with physical expectation and past observation, more rapid convergence was noted for smaller ϵ_B and the less severely varying $\epsilon(r)$ functions. The same was often but not always found for increasing index, n.

While there is no reason why as many $F_{n,1}$ as are needed for the most slowly convergent $\epsilon_i/\epsilon_{\mathrm{eff}}$ sums (i.e., for $x \rightarrow 1$) could not be directly generated and stored, in practice it was found that sufficiently regular variation with n, relative to the unmodified (KW) theory coefficients, $F^0_{n,1}$, exists in the large-n regions to allow the former to be more rapidly and conveniently obtained by extrapolation from the latter. Consequently, the $F_{n,1}$ coefficients for all modifications and ω ($=\epsilon_B/\epsilon_i$) values over the range $n = 0$ to 20 were generated and stored and higher n-value coefficients obtained from the regular behavior of

$$Q_n = (\delta_n - \delta_{n-1})/(\delta_{n-1} - \delta_{n-2}) \qquad \text{(A6)}$$

where $\delta_n = F^0_{n,1} - F_{n,1}$.

It was generally ascertained that the root-mean-square ($\hat{Q}$) values obtained from the double-limit-derived (dld) $F_{n,1}$ values for $n = 10$ to 20 were in the range 0.90 to 0.95, with very little variation within a given case over n, as evidenced by the very small variances noted (<0.02). Furthermore, smaller $\hat{Q}$ values are generally associated with more extreme modification functions. The slight trends with n occasionally noted could be incorporated by simple variance based adjustments to $\hat{Q}$, apparently uniformly successfully within the limits otherwise imposed by dld coefficient precision, as judged by comparison with extended dld coefficient set (to $n = 50$) results.

Multiple extrapolations to obtain sufficient terms for slowly convergent sums might be expected to compound the numerical accuracy and stability problems ordinarily encountered upon long summations. The following procedure has therefore been adopted to define parameter range and $\epsilon_{\mathrm{eff}}/\epsilon_i$ significance limits. Summation with the unmodified (KW) model coefficients may be conveniently carried out simultaneously with those of the desired model modification, and upon convergence, which is, incidentally, *uniformly slower for the former*, directly compared to the analytical approximation results derivable therefor. Moreover, the unmodified coefficients, $F_{n,1}{}^0$ may also be obtained by extrapolations of the same type as eq A6. The difference among the ϵ_{eff} KW values obtained in these different ways, the general nature of which follows, should parallel and because of the noted slower convergences magnify any uncertainties to which the modified model results should be subject.

Only for large x (both sites very near the cavity edge) are many sum terms needed for convergence, and only for $x > 0.95$ are there significant differences observed among the analytic and 20- and 50-basis coefficient sum results, with differences among the latter as large as between either of them and the former. The order of magnitude of these differences may be ~1% of ϵ_{eff} for p–p interactions and somewhat larger for p–d cases, but always, as far as the tests have been extended, as likely due to rounding of the leading (small n) $F_{n,1}$ coefficients, carried to 1 part in 10^{-5} (vide supra), as to the extrapolation in the large n range. Interestingly, much less dependency on evaluation method is found for geometries characterized by smaller θ, likely entirely due to the more rapid convergence forced by the spherical harmonic factors. There seems to be little dependence upon ϕ as long as geometries where $\Delta W \rightarrow 0$, i.e., the ϵ_{eff} discontinuity regions, are avoided.

Among the modified model results, generally smaller differences with basis set lengths and extrapolation method are observed, with the smallest usually noted for the most gradually varying $\epsilon(r)$ functions. This result is likely due to the more rapid convergence obtained with the smaller $F_{n,1}$ coefficients, against an absolute ϵ_{eff} threshold (i.e., two successive changes between terms of differing sign of less than 0.005).

Consequently, we may conclude for present purposes, where limiting boundary configurations are not at issue, that the simplest procedure (20-term basis with extrapolation) can provide sufficiently accurate absolute and relative ϵ_{eff} values, and it is these which are herein reported.