

Contributions from Dielectric Inhomogeneity to the Free Energy of Ionic Solvation

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Abstract

A new dielectric profile for the solvent dielectric constant beyond the primary coordination or solvation sphere is used to show that neglect of dielectric inhomogeneity by the Born treatment can lead to significant overestimation of ionic solvation energies.

Theoretically rigorous treatments of the energetics of ionic solvation must await further developments of molecular models which combine the techniques of quantum and statistical mechanics.¹⁻³ Treatments which model the solvent as a dielectric continuum show that the dominant contribution to the free energy of solvation of a monatomic ion is given by the difference between the work of charging the ion in the solvent and in vacuum.⁴ It has been found that the Born theory,⁵ in which the dielectric is homogeneous up to a poorly defined⁶ ionic boundary, seriously overestimates the work of charging.⁴ If partitioning of the solvent into primary, secondary and bulk regions⁷⁻⁹ is accepted the short-comings of the Born model can be attributed to the very low dielectric permittivity of the primary shell. In the present analysis we employ a continuum model to investigate the impact of dielectric inhomogeneity on the energetics of solvation of the primary ion.

Disregarding physically unrealistic models^{10,11} which invoke discontinuities in the dielectric profile $\epsilon(r)$, we find that, although a large fraction of the solvation energy of the primary ion comes from the secondary region where the dielectric is not homogeneous, the current view^{12,13} appears to be that the contribution from the inhomogeneous

¹ Kistenmacher, H., Popkie, H., and Clementi, E., *J. Chem. Phys.*, 1974, **61**, 799.

² Watts, R. O., Clementi, E., and Fromm, J., *J. Chem. Phys.*, 1974, **61**, 2550.

³ Corongiu, G., and Clementi, E., *J. Chem. Phys.*, 1978, **69**, 4885.

⁴ Bockris, J. O'M., and Reddy, A. K. N., 'Modern Electrochemistry' Vol. 1, pp. 45-174 (Plenum: New York 1970).

⁵ Born, M., *Z. Phys.*, 1920, **1**, 45.

⁶ Stokes, R. H., *J. Am. Chem. Soc.*, 1964, **86**, 979.

⁷ Bernal, J. D., and Fowler, R. H., *J. Chem. Phys.*, 1933, **1**, 515.

⁸ Frank, H. S., and Wen, W. Y., *Discuss. Faraday Soc.*, 1957, **24**, 133.

⁹ Saluja, P. P. S., 'International Review of Science, Physical Chemistry Series Two' Vol. 6, pp. 1-51 (Butterworths: London 1976).

¹⁰ Beveridge, D. L., and Schnuelle, G. W., *J. Phys. Chem.*, 1975, **79**, 2562.

¹¹ Abraham, M. H., Liszi, J., and Mészáros, L., *J. Chem. Phys.*, 1979, **70**, 2491.

¹² Buckingham, A. D., *Discuss. Faraday Soc.*, 1957, **24**, 151.

¹³ Goldman, S., and Bates, R. G., *J. Am. Chem. Soc.*, 1972, **94**, 1476.

geneity itself is negligible. This being the case, we would expect the free energy of charging a primary solvated ion to be accurately represented by the Born energy⁵

$$W_B = \frac{q^2}{2(4\pi\epsilon_0)a} \left(\frac{1}{\epsilon_b} - 1 \right) \quad (1)$$

where q is the charge of the primary ion of radius a , ϵ_0 is the permittivity of free space and ϵ_b is the relative permittivity of the bulk solvent.

With the aid of a new dielectric profile $\epsilon(r)$ which describes the radial dependence of the relative dielectric permittivity we now show that corrections for the influence of dielectric inhomogeneity on the results from the Born expression are small but certainly not, in general, negligible. The new profile is empirical but for this very reason is broader in scope than most previous profiles based on special mechanisms, such as dielectric saturation, for the inhomogeneity. If ligand-solvent and solvent-solvent intermolecular forces are considered it becomes clear that dielectric inhomogeneity is not exclusively determined by electric saturation as most previous models^{12,14,15} have assumed. In the present model the dielectric profile, $\epsilon(r)$, for the secondary region varies continuously and monotonically between the value ϵ_a at $r = a$ and ϵ_b at $r = b$. The derivative $\epsilon'(r)$ at the boundary between the secondary and bulk regions is also continuous. Our profile (see Fig. 1) takes the simple form

$$\epsilon(r) = \epsilon_a(\epsilon_b/\epsilon_a)^{f(r)} \quad a \leq r \leq b \quad (2a)$$

where the exponent

$$f(r) = 1 - [(b-r)/(b-a)]^2 \quad (2b)$$

varies between zero where $r = a$ and unity where $r = b$. Beyond $r = b$ the permittivity of the solvent maintains the constant bulk value ϵ_b .

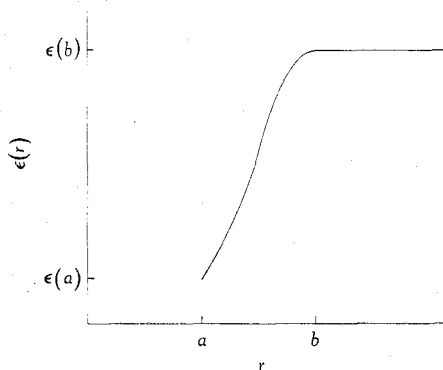


Fig. 1. Profile of the relative dielectric permittivity $\epsilon(r)$ beyond the primary ion as a function of the radial distance r from the ionic centre.

Provided that the ionic strength is sufficiently small the electrostatic field $E(r)$ outside the ion satisfies the Maxwell equation

$$\nabla \cdot \epsilon(r) E(r) = 0 \quad (3)$$

At all points beyond the primary ion the electrostatic field $E(r)$ is therefore given by

$$E(r) = [1/(4\pi\epsilon_0)][q\hat{r}/\{\epsilon(r)r^2\}] \quad (4)$$

where \hat{r} is the unit vector directed radially outwards along the position vector r . Despite recent suggestions to the contrary¹¹ both the energy density and reaction

¹⁴ Laidler, K. J., and Pegis, C., *Proc. R. Soc. London, Ser. A*, 1957, **241**, 80.

¹⁵ Laidler, K. J., and Muirhead-Gould, J. S., *Trans. Faraday Soc.*, 1967, **63**, 953.

field¹⁶ techniques, when correctly applied, show that the electrostatic contribution to the free energy of solvation is¹⁵

$$W = \frac{1}{(4\pi\epsilon_0)} \frac{q^2}{2} \int_a^\infty \left[\frac{1}{\epsilon(r)r^2} - \frac{1}{r^2} \right] dr \quad (5)$$

For the dielectric profile (2) we find

$$W = \frac{1}{(4\pi\epsilon_0)} \frac{q^2}{2} \left[\frac{1}{b\epsilon_b} - \frac{1}{a} + \frac{1}{\epsilon_a} \int_a^b \left(\frac{\epsilon_a}{\epsilon_b} \right)^{f(r)} r^{-2} dr \right] \quad (6)$$

As expected, this expression degenerates to the Born equation (1) as the width of the secondary shell shrinks to zero. It also reduces to the Born result when the dielectric constant ϵ_a tends towards the bulk value ϵ_b . Table 1 lists ratios of the electrostatic energy (6) to the Born counterpart (1) for typical values of the permittivity ϵ_a at the periphery of the primary solvated ion, the bulk dielectric permittivity ϵ_b of the solvent and of the ratio a/b of the primary to secondary ionic radii. These results suggest that the correction to the Born energy from dielectric inhomogeneity often represents an appreciable percentage of the free energy of solvation of the primary ion.

Table 1. Ratios of electrostatic stabilizations W of primary ions in an inhomogeneous dielectric to the corresponding Born stabilizations W_B for a homogeneous dielectric

Two values of the dielectric permittivity ϵ_a at the boundary of the primary ion are considered. The ratios are tabulated as functions of the bulk permittivity ϵ_b and of the quotient, a/b , of the primary and secondary radii

ϵ_a	ϵ_b	W/W_B for a/b values of				ϵ_a	ϵ_b	W/W_B for a/b values of			
		0.2	0.4	0.6	0.8			0.2	0.4	0.6	0.8
2	5	0.83	0.90	0.95	0.98	3	5	0.92	0.95	0.97	0.99
2	10	0.82	0.90	0.94	0.98	3	10	0.89	0.94	0.97	0.98
2	20	0.83	0.91	0.95	0.98	3	20	0.89	0.94	0.97	0.99
2	40	0.84	0.91	0.95	0.98	3	40	0.89	0.94	0.97	0.99
2	80	0.85	0.92	0.96	0.98	3	80	0.90	0.95	0.97	0.99

Because the solvation energy of the primary ion is itself a large fraction of the total solvation energy of the bare ion we conclude that dielectric inhomogeneity beyond the primary coordination or solvation sphere is significant whenever the thickness of the secondary region is comparable to or larger than the radius of the primary sphere. Although the present analysis is based on a special choice of dielectric profile it is interesting to note that results similar to those in Table 1 are maintained when our exponential profile for the dielectric permittivity in the secondary region is replaced by a rectilinear profile of the form

$$\epsilon(r) = \alpha r + \beta$$

This observation suggests that our conclusion is not particularly sensitive to the assumed form of the inhomogeneity.

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¹⁶ Kirkwood, J. G., *J. Chem. Phys.*, 1934, **2**, 351.