Research Article

A short Note on Dielectric Saturation and Born Radii

Juan S. Gómez-Jeria*, Demian Morales-Lagos

Quantum Pharmacology Unit, Department of Chemistry, Faculty of Sciences, University of Chile. Las Palmeras 3425, Santiago 7800003, Chile
*Corresponding Author: Juan S. Gómez-Jeria, facien03@uchile.cl

Abstract A formal expression for the electrostatic contribution to the chemical potential is discussed. A function describing the variation of the dielectric constant with the distance from the ion is analyzed. It is concluded that in the regions of the solvent presenting an ideally complete saturation of the orientational polarizability, the entropic destabilization is exactly counterbalanced by the enthalpic stabilization of the solvent. The only contributions are those coming from those regions where thermal agitation hinders the alignment of the solvent's dipoles in the solute's dielectric displacement. It is suggested that Born radius is a way of incorporating dielectric saturation as a radial increment.

Keywords Chemical potential, orientational polarizability, dielectric constant, Born radius, dielectric saturation

Introduction

The chemical potential of solvation (CPS) governs the degree of spontaneity of the dissolution process. For ionic solvation, the main contribution to CPS is of electrostatic nature. By analyzing solvation thermodynamics by means of classical electrostatics (Reaction Field Theory, RFT) [1], we derived the following general expression for the electrostatic contributions to CPS, $\Delta\mu_{el}$, for the case of unpolarizable ionic solutes [2, 3]:

$$\Delta\mu_{el} = \frac{Q^2}{2N_0} \int_{r_0}^{\infty} \frac{d\varepsilon^{-1}(r)}{r} \qquad (1)$$

where N_0 is the Avogadro's number, Q is the ion net charge assumed to be punctual and centered in an empty spherical cavity of radius r_0 and ε® is a function to be specified describing the variation of the dielectric constant with the distance to the ion when final equilibrium is attained. Eq. 1 can be applied to ideal dilute solutions under isothermic and isobaric conditions. Its inspection shows a quadratic dependence upon the charge. In addition, it predicts that large variations of ε near the ion facilitate the dissolution process. Those regions presenting a constant ε do not contribute to $\Delta\mu_{el}$.

On the other hand, it is known that Born Equation (BE) considers the solvent as a continuous dielectric medium characterized by the macroscopic dielectric constant of the pure solvent, ε_b, giving the following expression for $\Delta\mu_{el}$ [4]:

$$\Delta\mu_{el} = -\frac{Q^2}{2N_0}\left[1-\frac{1}{\varepsilon_b}\right]\frac{1}{r_0} \qquad (2)$$

It can be shown that BE is a particular limit case of Eq. 1 arising from the discontinuity of ε at r_0. Then, in the RFT framework, BE is the upper bound to $|\Delta\mu_{el}|$ because it maximizes the gradient of ε and minimizes the distance between the ion and the largest ε derivative value.

Physical arguments led to consider the ε(r) function shown in Fig. 1 [2, 3, 5].
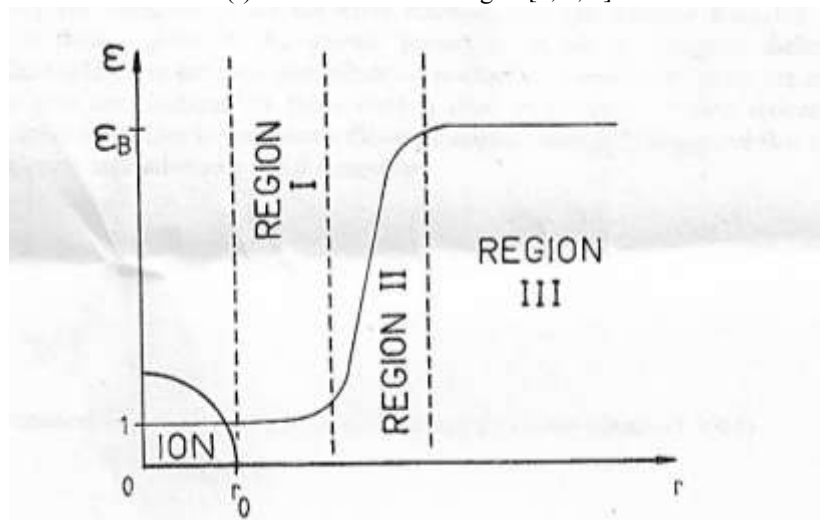

Figure 1: Plot of ε against the distance to the ion showing Regions I, II and III

This function shows three main regions, named I, II and III. Region I is absent when the solvent polarity and/or the ionic charge are small. The foregoing discussion is restricted to non-associated, very polar solvents displaying only orientational polarization and at the limit of a high ionic charge. Region I has an ideally complete dielectric saturation of the orientational polarizability (DSOP) neglecting electrostriction. In Region II, the orienting effect of the solute's dielectric displacement and the disorganizing effect of thermal agitation compete. In Region III, the effect of the solute on the solvent is negligible.

For the physical situations described by this model, only region II contributes to Eq. 1. Region III is not affected by the insertion process due to the screening of the solute's dielectric displacement by the internal regions. On the other hand, the fact that region I does not contribute to $\Delta\mu_{el}$ because it has a constant ε is an unexpected conclusion. The only way to preserve the internal coherence of the model is by suggesting that in those regions of the solvent presenting an ideally complete DSOP, the entropic destabilization (produced by the antiparallel dipole alignment of the solvent), is exactly counterbalanced by the enthalpic stabilization of the solvent dipoles. This implies that $\Delta\mu_{el}=0$ in Region I. This model may be useful to understand liquid crystals and ferroelectric materials because they present a high orientational polarizability.

The analysis of Region II suggests that the directing forces determining the degree of spontaneity of ionic solvation are regulated by the balance of thermal agitation effects (identified to an enthalpic term), and the dominant effect of the orientation of the solvent's dipoles in the field (attributed to the enthalpic term). The effects of small variations of the temperature on $\Delta\mu_{el}$ may be easily visualized in terms of the abovementioned equilibrium and Fig. 1. Fir rigid solvent molecules, the change in the dipole alignment with increasing temperature affects Region II but not Region I. This induces a shift of the outer limit of Region II toward the ion, increasing the slope of the curve (see Fig. 1). Therefore, according to Eq. 1, the solubility raises. This analysis is valid for solvents fulfilling the condition $(\partial\varepsilon/\partial T)_P=0$. For the other cases, a lowering or a rising of $(\partial\varepsilon/\partial T)_P$ raises or lowers ε_B respectively. This has an

additional but weak effect upon the gradient of region II that can be included for each particular case. Even if ε_B changes with temperature, it remains constant in Region II.

For processes of ionic dissolution under isothermic and isochoric conditions the above reasoning can be applied by considering the Helmholtz free energy, internal energy and entropy state functions. Another important consequence of Eq. 1 regards the physical interpretation of the Born radius, r_B [6, 7]. The application of BE using crystalline radii systematically overestimates the experimental value of $\Delta\mu_{el}$ [8]. It has been shown that the parameterization of r_0 in Eq. 2 giving r_B ($r_B > r_0$) provides surprisingly good results. At present, the physical meaning of r_B and its dependence upon the temperature and the charge of the solute are the subject of discussion [9].

As a first approach to the understanding of this problem, we shall consider the unipolar term of Beveridge and Schnuelle's model [10]. This model considers a spherical ion with radius r_0 surrounded by a dielectric layer of thickness Δr_0 and permittivity ε_B. This model considers a spherical ion with radius r_0 surrounded by a dielectric layer of thickness Δr_0 and permittivity ε_{II}, embedded in an infinite dielectric characterized by ε_B. Their Modified Born Equation is also a particular case of Eq. 1 because of the discontinuities of ε in the surfaces limiting the dielectrics (Eq. 40 with n=0 in Ref. 10). Assuming an ideally complete DSOP in the local dielectric region (i.e., $\varepsilon_{II} \longrightarrow 1$), together with complete screening of the solute's dielectric displacement (i.e., the external region is not affected), it is possible to recover Eq. 2 in which r_0 was replaced by $r_0 + \Delta r_0$. We identify this last expression as the Born radius. This immediately suggests that r_B is principally a consequence of the microscopic phenomenon called dielectric saturation and that Δr_0, depending upon Q, can be interpreted as the limit of the average extent of the DSOP. Mathematically, the Born radius is the a way of incorporating dielectric saturation as a radial increment and not as a reduction of ε. Solvents with $(\partial\varepsilon/\partial T)_P \approx 0$ will show a decrease of Δr_0 with raising temperature. This effect will be more noticeable for flexible solvent molecules. Within this context, the empirical values of r_B are theoretically important because they contain information concerning the real importance of dielectric saturation as the determining factor for the microscopic structure of the solvent in the ion's vicinity. The, even when ε is a macroscopic mean value, the statement that "dielectric saturation and a charge-dependent Born radius are two manifestations of the same phenomenon at a microscopic level" is erroneous [9]. In addition, it is expected that Δr_0 should be small for anions because dielectric saturation is higher due to the smaller charge/radius ratio.

This analysis can be generalized for prolate spheroidal ions, starting from [5]:

$$\Delta\mu_{el} = -\frac{Q^2}{2N_0 d} \int_{\lambda_0}^{\infty} \ln\left[\frac{1+\lambda}{1-\lambda}\right] d\varepsilon^{-1}(\lambda) \qquad (3)$$

where 2d is the interfocal distance and λ the prolate coordinate describing surfaces with this symmetry. The oblate spheroidal case is analogous to Eq. 3, but replacing the natural logarithm by $\cot^{-1}(\lambda)$. The results are similar. Finally, the above analysis can be strictly applied to higher order multipoles even when DSOP is absent or small.

References

[1]. Böttcher, C. J. F. *Theory of Electric Polarization*. Elsevier Publishing Company: Amsterdam, 1973.

[2]. Gomez-Jeria, J. S.; Morales-Lagos, D. Free energy of a charge distribution in a spheroidal cavity surrounded by concentric dielectric continua. *Journal of Physical Chemistry* 1990, 94, 3790-3795.

[3]. Morales-Lagos, D. Master in Chemistry Thesis. University of Chile, Santiago, Chile, 1993.

[4]. Born, M. Volumen und hydratationswärme der ionen. *Zeitschrift für Physik* 1920, 1, 45-48.

[5]. Morales-Lagos, D.; Gomez-Jeria, J. S. New developments in the continuum representation of solvent effects. *Journal of Physical Chemistry* 1991, 95, 5308-5314.

[6]. Stokes, R. The van der Waals radii of gaseous ions of the noble gas structure in relation to hydration energies. *Journal of the American Chemical Society* 1964, 86, 979-982.

[7]. Hirata, F.; Redfern, P.; Levy, R. M. Viewing the Born model for ion hydration through a microscope. *International Journal of Quantum Chemistry* 1988, 34, 179-190.

[8].   Noyes, R. M. Thermodynamics of ion hydration as a measure of effective dielectric properties of water. *Journal of the American Chemical Society* 1962, 84, 513-522.

[9].   Roux, B.; Yu, H. A.; Karplus, M. Molecular basis for the Born model of ion solvation. *Journal of Physical Chemistry* 1990, 94, 4683-4688.

[10].   Beveridge, D. L.; Schnuelle, G. W. Free energy of a charge distribution in concentric dielectric continua. *Journal of Physical Chemistry* 1975, 79, 2562-2566.