The Shielding of the solvating electron in an electrolyte

O.V.Vasil'ev, V.D.Lakhno
The Biological Research Centre, USSR Academy of Sciences, Pushchino
Computer Centre, Puschchino

ABSTRACT. A theory of the shielding of the solvated electron in dilute solution of a strong electrolyte whose ions are fairly inert in relation to the solvated electron is proposed. The consequences of the ionic mechanism of localisation are discussed. In particular, the shift of the absorption band maximum of the solvated electron with increase in the ionic strength of the solution is interpreted.

The Debye—Hückel theory,[1] developed in relation to classical ions, cannot be used directly in the description of the shielding of the solvated excited electron in solution. On the other hand, the known models of the solvated electron describe only its interaction with the pure solvent and it is therefore necessary to extend them to the case of a solution with a non-zero ionic strength. Such a generalisation has been achieved[2] for the polaron model. In this study we do not make the model specific and only certain model-independent consequences are deduced.

We shall suppose that the problem of the solvated electron reduces to a one-electron problem—to a non-linear Schrödinger equation:

$$(\hat{H}[\Psi]-E)\,\Psi=0. \tag{1}$$

The energy is given by $E[\Psi] = \int dV\Psi^*\hat{H}[\Psi]\Psi$. We introduce a functional $F[\Psi]$ such that

$$\delta F/\delta\Psi^*=2\hat{H}\Psi. \tag{2}$$

For the moment we postulate that F is independent of temperature: $\partial F/\partial T = 0$. This means that we assume that there exists a comparatively simple model of the localised electron in which the solution of the problem of the minimum in the functional $F[\Psi]$, subject to the normalisation $\int dV|\Psi|^2 = 1$, yields Eqn. (1), while F generated by the solutions of this equation is the free energy of solvation. {The energy $E[\Psi_d]$ and the free energy $F[\Psi_d]$ of the delocalised state Ψ_d should be zero.}

An example of such a model is Pekar's polaron:[3,4]

$$\hat{H}[\Psi] = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{4\pi\varepsilon_0\varepsilon}\int dV'\frac{|\Psi(r')|^2}{|r-r'|}, \tag{3}$$

$$F[\Psi] = \frac{\hbar^2}{2m}\int dV|\nabla\Psi|^2 - \frac{e^2}{8\pi\varepsilon_0\varepsilon}\iint dV\,dV'\frac{|\Psi(r)|^2|\Psi(r')|^2}{|r-r'|} \tag{4}$$

where we put for the moment $d\varepsilon/dT = 0$ and $dm/dT = 0$. Here m is the effective mass of the electron, $\varepsilon = (\varepsilon_d^{-1}-\varepsilon_s^{-1})^{-1}$, ε_d and ε_s are the optical and static dielectric permittivities of the solvent, ε_0 is the dielectric constant, and e is the charge of the proton.

We now return to the general problem (1)—(3). We assume that a strong electrolyte, whose ions are fairly inert in relation to the solvated electron during its lifetime (this does happen—see Pikaev and Kabakchi[5]), is dissolved in a liquid. Eqn. (1) then must be replaced by the expression

$$(\hat{H}[\Psi]-e\Phi[\Psi]-E)\,\Psi=0, \tag{5}$$

in which the potential Φ, generated by the ions, obeys the Poisson—Boltzmann equation adjusted for self-consistency:

$$\Delta\Phi = -\frac{e}{\varepsilon_0\varepsilon_s}\sum_j n_j z_j \exp\left(-\frac{z_j e}{k_B T}(\Phi+\Phi_e[\Psi])\right), \tag{6}$$

$$\Phi_e = -\frac{e}{4\pi\varepsilon_0\varepsilon_s}\int dV'\frac{|\Psi(r')|^2}{|r-r'|}, \tag{7}$$

where n_j is the concentration of ions with the charges ez_j (the electroneutrality condition is

$$\sum_j n_j z_j = 0\,);$$

Φ is the potential generated by the ions, and k_B is the Boltzmann constant. The functional of the electron energy is

$$E[\Psi] = \int dV\,\Psi^*\hat{H}[\Psi]\Psi - e\int dV\,\Phi[\Psi]|\Psi|^2. \tag{8}$$

The functional F is replaced by the following functional:

$$F_{tot}[\Psi,\,\Phi]=F[\Psi]+F_{ion}[\Psi,\,\Phi], \tag{9}$$

where

$$F_{ion} = -\frac{\varepsilon_0\varepsilon_s}{2}\int dV(\nabla\Phi)^2 -$$

$$-T\sum_j n_j\int dV\left[\exp\left(-\frac{z_j e}{k_B T}(\Phi+\Phi_e[\Psi])\right)-1\right]. \tag{10}$$

The problem of determining the extremum in the functional $F_{tot}[\Psi,\Phi]$ subject to the normalisation of Ψ, is equivalent to the problem defined by Eqns. (5)—(7).

The functional $F_{tot}[\Psi,\Phi]$ and the total energy functional:

$$E_{tot}[\Psi,\,\Phi]=E[\Psi]+\frac{\varepsilon_0\varepsilon_s}{2}\int dV(\nabla\Phi)^2, \tag{11}$$

form what is "almost the Gibbs—Helmholtz equation"

$$E_{tot}=F_{tot}-TdF_{tot}/\partial T, \tag{12}$$

in which Ψ and Φ (arguments of the functional F_{tot}) cannot be differentiated with respect to temperature. At the extremum of the functional $F_{tot}[\Psi,\Phi]$, this equation is converted into the true Gibbs—Helmholtz equation

$$E_{tot}=F_{tot}-TdF_{tot}/dT. \tag{13}$$

The functional F_{ion} represents the electrostatic free energy for the non-linear Poisson—Boltzmann equation [Eqn. (6)],[2,6] while the functional F_{tot} represents the free energy of the entire system. If $d\varepsilon_s/dT \neq 0$, then the expression for the energy E_{tot} changes in conformity with Eqn. (13).[7]

Evidently, an increase in the ionic strength of the solution increases the stability of the localised state:

$$\frac{dF_{tot}}{dn} = -\frac{TN}{n} < 0, \tag{14}$$

where

$$N = \sum_j n_j \int dV \left[\exp\left(-\frac{z_j e}{k_B T}(\Phi + \Phi_e[\Psi]) \right) - 1 \right],$$ (15)

is the change in the number of ions induced by the localisation of the electron, while the concentration parameter n is introduced by means of the equations

$$n_j = k_j n, \qquad \sum_j k_j z_j = 0.$$ (16)

The ionic contribution to the localisation is order-generating: it can be shown that, if one puts $d\varepsilon_s/dT = 0$, then [subject to the electroneutrality conditions (16)], the entropy S is negative:

$$S = -dF_{tot}/dT < 0.$$ (17)

The question arises how strong is the ionic mechanism of the localisation. Evidently, at high concentrations of ions (several moles per litre) the model (5)–(7) ceases to operate. However, in order to gain a qualitative (and model-independent) idea about the kind of contribution that ionic shielding makes to the localisation of the electron, one may abandon this factor and consider the limit $n \to \infty$. In this limit, $\Phi[\Psi] = -\Phi_e[\Psi] = (\varepsilon/\varepsilon_s)\Phi_p[\Psi]$, where $\Phi_p[\Psi]$ is the potential of Pekar's polaron [see Eqn. (7) and Eqns. (3) and (4)]. In the usual solvents with $\varepsilon_s \gg \varepsilon_d$ the effect of ionic shielding is weaker than that of the polarisation of the solvent.

The linearisation approximation analogous to the usual Debye–Hückel theory [expansion of the exponential function in Eqns. (6) and (10)] makes it possible to write

$$S = -N < 0,$$ (18)

$$\Phi[\Psi] = \frac{e}{4\pi\varepsilon_0\varepsilon_s} \int dV' \frac{|\Psi(r')|^2}{|r-r'|} \left[1 - \exp\left(-\frac{|r-r'|}{r_D} \right) \right],$$ (19)

$$F_{ion}[\Psi] = -$$

$$-\frac{e^2}{8\pi\varepsilon_0\varepsilon_s} \int\int dV\,dV' \frac{|\Psi(r)|^2|\Psi(r')|^2}{|r-r'|} \left[1 - \exp\left(-\frac{|r-r'|}{r_D} \right) \right],$$ (20)

where $r_D = (1/e)(\varepsilon_0\varepsilon_s k_B T/I)^{1/2}$ is the Debye radius and $I = \sum_j n_j z_j^2$ is the ionic strength. The linearisation approximation can be exact or inexact at low concentrations depending on the kind of functional of Ψ which has to be found. At high concentrations, this approximation becomes exact [see Eqn. (6)]. It follows from Eqn. (20) that

$$F_{tot} = \lim_{n\to\infty} F_{tot} + \frac{k_B T}{2I} \int dV |\lim_{n\to\infty} \Psi(r)|^4 + o\left(\frac{1}{I}\right).$$ (21)

In the limit $n \to 0$ in the region of the "small electron radius", i.e.

$$\langle r \rangle = \int dV\, r\, |\Psi|^2 \ll r_D,$$ (22)

we obtain the usual Debye–Hückel theory:

$$F_{tot} = \lim_{n\to\infty} F_{tot} - 2k_B T N + o(I^{1/2}),$$ (23)

$$E_{tot} = \lim_{n\to\infty} F_{tot} - 3k_B T N + o(I^{1/2}),$$ (24)

$$E = \lim_{n\to 0} F - 4k_B T N + o(I1.2),$$ (25)

$$k_B T N = \frac{e^3}{16\pi} \left(\frac{I}{k_B T(\varepsilon_0\varepsilon_s)^3} \right)^{1/2}.$$ (26)

On absorption of a light quantum, the solvated electron c migrate either into the conductivity band or into an excited $(c$ adjusted for self-consistency) localised state. In the former case u absorption energy W is $-E$, while in the latter it is $W = E_{-e}$ where the energy $\tilde{E}$ of the excited state Ψ_1 in the potential well the ground state Ψ_0 is given by the linear Schrödinger equation

$$(\hat{H}[\Psi_0] - e\Phi[\Psi_0] - \tilde{E})\Psi_1 = 0.$$ (*

The deviation of the $W(I)$ relation at low values of I from Eq. (25), i.e.

$$W = W|_{I\to0} + \varkappa I^{1/2},$$

where

$$\varkappa = \frac{e^3}{4\pi}(k_B T(\varepsilon_0\varepsilon_s)^3)^{-1/2},$$ (*

may be a sign of the transition to the excited state (at 300 K at $\varepsilon_s = 80$, we have $\varkappa = 0.04$ eV M$^{-1/2}$). Low values of I are define: by Eqn. (22) or, if one assumes that $\langle r \rangle \simeq 3$ Å and $T \simeq 300$ K they are defined by the condition $I \ll (\varepsilon_s/40)$ M.

Data are available for solvated electrons in solutions of MgC_2 LiClO$_4$, and LiCl in water and of LiCl in heavy water;[8,9] w: increase in the concentration of ions, a hypsochromic shift of th absorption band is indeed observed [see Eqn. (25)]. The characteristic quantity 0.04 eV for $I \simeq 1$ M agrees with the experimental value. However, the data of Kreitus and co-workers[represent values of W scattered over the range $I \simeq 0-5$ M w: most values $\sim 1/2M$ and it is therefore difficult to reach a conclusio: on their basis concerning the $W(I)$ relation for low values of I. The polaron model defined by Eqns. (3) and (4) is qualitatively consiste: with the experimental relation $W(I)$ only in the range from 0 t 3 M.[2] However, a rigorous correspondence between the descriptio: based on Eqns. (5)–(7) for any model $\hat{H}[\Psi]$ and the experiment: relation $W(I)$ can apparently be expected only for low values c: I: $I \ll (\varepsilon_s/40)$ M.

We may note in conclusion that the possible shift of the conductivity band as I changes[9] does not affect our discussion.

References

1. P Debye, E Hückel *Phys. Z.*, 1923, **24** 185
2. O V Vasil'ev, V D Lakhno *Termodinamicheskaya Teoriya Sol'vatirovannogo Elektrona* (Thermodynamic Theory of the Solvated Electron), Preprint from the Biological Research Centre, USSR Academy of Sciences, Pushchino, 1990
3. S I Pekar *Zh. Eksp. Teor. Fiz.*, 1946, **16**(3) 341
4. M F Deigen *Zh. Eksp. Teor. Fiz.*, 1954, **26**(2) 300
5. A K Pikaev, S A Kabakchi, Handbook, *Reaksionnaya Sposobnost' Pervichnykh Produktov Radioliza Vody* (The Reactivity of the Primary Products of the Radiolysis of Water), Energoatomizdat, Moscow, 1982
6. K A Sharp, B Honig *J. Phys. Chem.*, 1990, **94** 7684
7. I P Bazarov *Termodinamika* (Thermodynamics), Vys. Shkola. Moscow, 1976
8. I V Kreitus *J. Phys. Chem.*, 1985, **89** 1987
9. I V Kreitus, D A Strode *Khim. Vys. Energii*, 1989, **23**(3) 218