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II–**electrophoresis of deoxyhemoglobin** S
Theoretical study of the volume variation and electrocalorific effect

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Abstract

In the first part of this work by Olatunji and Ayeni [1]***, we consider the deformation of HbS molecule without volume variation during the electrophoresis process. In this second part, we consider the inverse case where the ellipsoid do not change the form but only his volume changes. We also consider the induced electro calorific effect. The results obtains are:***

$$V - V_0 = \frac{VE^2}{8\pi}\left[\left(\frac{f}{g}\right)\beta_x - \frac{h\beta_x(\varepsilon_x - 1)(\varepsilon_x + 2) + k\beta(\varepsilon - 1)(\varepsilon + 2)}{3g^2}\right]$$

$$Q - Q_0 = \frac{TVE^2}{8\pi}\left[\left(\frac{f}{g}\right)\chi_x - \frac{h\chi_x(\varepsilon_x - 1)(\varepsilon_x + 2) + k\chi(\varepsilon - 1)(\varepsilon + 2)}{3g^2}\right] w$$

here β_x ***and*** χ_x ***are the isothermal coefficient of compressibility and the coefficient of thermal dialation of the molecule,β and χ the corresponding coefficients for the solvent. (f,g,h,k) are analytical functions which depend on dielectric constants and coefficient of depolarization*** A_x***.***

Keyword: Hemoglobin S, Volume Variation, electrocalorific Effect

1.0 The theoretical model

We have seen in the first paper [1] that the volume variation in a deformation is given by the sum u_{ii}. If this sum is equal to zero the volume is unchanged (sliding), only the form changes. Hence the hemoglobin S (HbS) molecule [2] stretched becomes an elongated ellipsoid of revolution with eccentricity *e*.

In this second part, we consider the inverse problem where the form of the ellipsoid remain constant, and only his volume varies (uniform compression) Consequently, the free energy is reduced to the electrostatic component [3]. Viz:

$$\psi = \psi_0 - \frac{VE^2}{8\pi}\frac{(\varepsilon_x - 1)\varepsilon}{[\varepsilon + (\varepsilon_x - \varepsilon)A_x]} \qquad (1.1)$$

were ψ_0 is the body energy when the electric field is removed, ε_x the dielectric constant of the ellipsoid along x axis, E the strength of the constant external field applied along this axis, V the volume of the body in the body in the field, V_0 his volume when the field is removed, and A_x the coefficient of depolarization (or factor form), ε the dielectric constant of the medium in which the electrophoresis is performed (acetate buffer pH 6,2 on agar).

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For a elongated ellipsoid we have the approximation:

$$A_x = \frac{1}{3} - \frac{4}{15}\left(\frac{a_1 - a_2}{a}\right)^2 \quad a_1 > a_2 > 0 \tag{1.2}$$

where a_1 and $a_2 = a_3$ the semiaxes of the ellipsoid respectively, and a the radius of the sphere. In the first paper [1], we have introduced the parameter ς characterizing the deformation, viz:

$$\varsigma = \left(\frac{a_1 - a_2}{a}\right) \tag{1.3}$$

Written that the total free energy is minimum. We have obtained the analytical expression of the distortion ς interm of experimental data viz:

$$\varsigma = \frac{9E^2}{40\pi\mu}\varphi(\varepsilon_0, \varepsilon) \tag{1.4}$$

with

$$\varphi(\varepsilon_0\varepsilon) = \frac{\left[(\varepsilon_0 - 1)(\varepsilon_0 - \varepsilon)\varepsilon + 5\gamma_1\varepsilon(1 + 2\varepsilon)/6\right]}{(\varepsilon_0 + 2\varepsilon)} \tag{1.5}$$

where ε_0 is the dielectric constant of the non distorted molecule, μ his slide modulus, and γ_1 an arbitrary parameter in the relation given the dielectric constant ε_x along x axis: [4]

$$\varepsilon_x = \varepsilon_0 + \frac{2\gamma_1}{3}\varsigma \tag{1.6}$$

We have also found that there exist a critical value for the field strength for which the deoxy-HbS molecule is destroyed:

$$E_c = \frac{4}{3}\sqrt{\frac{5\pi\mu}{\varphi(\varepsilon_0, \varepsilon)}} \tag{1.7}$$

In the sequel, we may also found that there also exist a critical value μ_c for the slide modulus μ, which indicates an upper limit for the deformability.

2.0 Derivation of the volume Variation $(V - V_0)$

For sake of simplicity let write ψ in the following form:

$$\psi = \psi_0 - \frac{VE^2}{8\pi}\left(\frac{f}{g}\right) \tag{2.1}$$

with

$$\begin{cases} f = (\varepsilon_x - 1)\varepsilon \\ g = \varepsilon + (\varepsilon_x - \varepsilon)A_x \end{cases} \tag{2.2}$$

We have by definition: [4]

$$V - V_0 = \left(\frac{\partial\psi}{\partial P}\right)_T \tag{2.3}$$

Using equation (2.1) the volume variation reads:

$$V - V_0 - \frac{VE^2}{8\pi}\left[\left(\frac{f}{g}\right)\beta_x - \frac{\partial}{\partial P}\left(\frac{f}{g}\right)\right] \tag{2.4}$$

where $\beta_x = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the isothermal coefficient of compressibility of the molecule. The evaluation of the second term in equation (2.4) is straight forward, and we obtain the following result:

$$V - V_0 - \frac{VE^2}{8\pi}\left[\left(\frac{f}{g}\right)\beta_x - \frac{h\left(\partial\varepsilon_x/\partial P\right)_T + k\left(\partial\varepsilon/\partial P\right)_T}{g^2}\right] \tag{2.5}$$

With the following definitions:

$$\begin{cases} h = \varepsilon\left[\varepsilon + (1-\varepsilon)A_x\right] \\ k = \varepsilon_x(\varepsilon_x - 1)A_x \end{cases} \tag{2.6}$$

It is worthy of note that this volume variation my be positive or negative (compression or uniform extension) with no change in volume.

3.0 Derivation of the electro calorific effect $(Q - Q_0)$

We have by definition [4]

$$Q - Q_0 = T(S - S_0) = T\left(\frac{\partial\psi)}{\partial T}\right)_P \tag{3.1}$$

Using equation (2.1) we get

$$Q - Q_0 = -\frac{VE^2}{8\pi}\left[\left(\frac{f}{g}\right)\chi_x + \frac{\partial}{\partial T}\left(\frac{f}{g}\right)\right] \tag{3.2}$$

where $\chi_x = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ is the thermal coefficient of distension of the molecule. Using the same method of calculation and previous notations we obtain:

$$Q - Q_0 - \frac{TVE^2}{8\pi}\left[\left(\frac{f}{g}\right)\chi_x - \frac{h\left(\partial\varepsilon_x/\partial T\right)_P + k\left(\partial\varepsilon/\partial T\right)_P}{g^2}\right] \tag{3.3}$$

It is worthy of note that the positive values of the electro calorific effect correspond the heat absorption.

4.0 Expressions for the electrostrictives constants

In this work we used the simplified formulae for the electrostrictives parameters. The exact formulae result from the (Density Fluctuation of the dielectric constant (DFDC) [5]

$$\left(\frac{\partial\varepsilon_x}{\partial P}\right)_T = \frac{\beta_x}{3}(\varepsilon_x - 1)(\varepsilon_x + 2) \tag{4.1}$$

$$\left(\frac{\partial\varepsilon_x}{\partial T}\right)_P = -\frac{\chi_x}{3}(\varepsilon_x - 1)(\varepsilon_x + 2) \tag{4.2}$$

$$\left(\frac{\partial\varepsilon}{\partial P}\right)_T = \frac{\beta}{3}(\varepsilon - 1)(\varepsilon + 2) \tag{43}$$

$$\left(\frac{\partial\varepsilon}{\partial T}\right)_P = -\frac{\chi}{3}(\varepsilon - 1)(\varepsilon + 2) \tag{4.4}$$

Using equation (4.1) and (4.2), the expression (2.5) and (3.3) giving the volume variation and the electro calorific effect read:

$$V - V_0 = \frac{VE^2}{8\pi}\Phi(\varepsilon_x, \varepsilon) \tag{4.5}$$

$$Q - Q_0 = -\frac{TVE^2}{8\pi}\psi(\varepsilon_x, \varepsilon) \tag{4.6}$$

where $\Phi(\varepsilon_x, \varepsilon) = \left[\left(\frac{f}{g}\right)\beta_x - \frac{h\beta_x(\varepsilon_x - 1)(\varepsilon_x + 2) + k\beta(\varepsilon - 1)(\varepsilon + 2)}{3g^2}\right]$ (4.7)

$$\psi(\varepsilon_x, \varepsilon) = \left[\left(\frac{f}{g}\right)\chi_x - \frac{h\chi_x(\varepsilon_x - 1)(\varepsilon_x + 2) + k\chi(\varepsilon - 1)(\varepsilon + 2)}{3g^2}\right] \quad (4.8)$$

At this stage of theoretical modeling, we observe that the physical parameters useful for the evaluation of *(V – V₀) and (Q – Q₀)* are:

- the strength *E* of the applied electric field
- the coefficients *(β_x, β)* of isothermal compressibility
- the coefficients *(χ_x, χ)* of isothermal distension
- the dielectric constants *(ε_x , ε_0, ε)*

We suppose at first approximation that the dielectric mediums crossed by the light are not absorbing mediums. Consequently, the Maxwell equation can be readily used :

- $\varepsilon_x = n_x^2$ for the dielectric constant of the ellipsoid along *x* axis
- $\varepsilon_0 = n_0^2$ for the dielectric constant of the sphere;
- $\varepsilon = n^2$ for the dielectric constant of the solution.

The strength of the applied field is an experimental data, that is not the case for the slide modulus μ of the deoxy-HbS. However, the value of this parameter can be readily estimated through the theoretical results derived by Cert [6] concerning the form fluctuations of elastic spherical molecule. Hence, the formulae giving the mean square of the deformation coefficients reads:

$$< (u_{ii})^2 > = \frac{kT}{3V\mu} \quad (4.9)$$

where (u_{ii}) are the diagonal elements of the deformation tensor, *k* the Boltzmann constant, *V* the volume of the molecule, ant *T* the absolute temperature. Moreover, in order to give more insight to small fluctuations cerf [5] used: :

$$< (u_{ii})^2 > \leq 0.01 \quad (4.10)$$

which leads to:

$$\mu \leq \mu_0 = \frac{100kT}{3V} \quad (4.11)$$

Consequently, for a spherical molecule of radius *a* we get the desired result viz : :

$$\mu_c = \frac{100kT}{4\pi a^3} \quad (4.12)$$

Introducing the polarizability *a* of the dielectric sphere with dielectric constant ε_0, in a solvent of dielectric constant ε, the radius *a* may be estimated using the following relationship [3]:

$$\alpha = a^3 \frac{\varepsilon_0 - \varepsilon}{\varepsilon_0 + 2\varepsilon} \quad (4.13)$$

5.0 Conclusion

An equation has been derived for the distortion of deoxy-HbS molecule during elctrophoresis. The distortion results from the equilibrium between the electrostatic and elastic free energies. [1]. In this process we consider that the volume of the molecule is constant.

In this work, we consider the inverse case where the form of the molecule remain unchanged, and only his volume varies. Consequently, we derived analytical expressions for this volume variation and the corresponding, electrocalorific effect in terms of thermodynamic and electrostrictives parameters.

As in the previous work, the equations presented here apply only to static field in dielectric medium.

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