

Free Energies of Electron Transfer, Electrochemical Properties, Electron Transfer Kinetic Theoretical and Quantitative Structural Relationship Studies of $C_n@X$ -[HbA] (HbA=Hemoglobin A; X= α - and β -Fumarate Crosslinked Hemoglobins (α XL & β XL)) Nanostructure Complexes

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ABSTRACT

The binding, release and oxidation of oxygen occur at the heme group iron ion. Hemoglobin oxidation-reduction studies have been previously performed using spectroelectrochemistry (SEC) and have provided insight into the hemoglobin electron transfer process and more specifically, into the heme group electronic factor and subunit interaction influences. In this study, the number of fullerene carbon atoms was used as an index to establish a relationship between the structures of hemoglobin A and α - and β -fumarate crosslinked hemoglobins, which were designated as HbA, α XL and β XL-[HbA] 1-3, respectively. These compounds represent the most well-known blood molecular systems and fullerenes (C_n , where $n = 60, 70, 76, 82$ or 86), which generated the following complexes: $C_n@[HbA]$, A-1 to A-5; $C_n@αXL$ -[HbA], B-1 to B-5 and $C_n@βXL$ -[HbA], C-1 to C-5. The relationship between the carbon atom number and electron transfer free energies (ΔG_{et}) were assessed using the Rehm-Weller equation for A-1 to A-5, B1 to B-5 and C-1 to C-5 supramolecular $C_n@X$ -[HbA] (where HbA = hemoglobin A; X = α - and β -fumarate crosslinked hemoglobins (α XL & β XL)) and complexes 4-57, which possessed different electrochemical properties. Calculations were presented for the first C_n oxidation potentials ($^{Ox}E_1$). The results were used to calculate the electron transfer first free energies ($\Delta G_{et(1)}$) of supramolecular complexes A-1 to A-5, B1 to B-5 and C-1 to C-5 for fullerenes C_{60} to C_{300} . The first free activation energies and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^\ddagger$ ($\Delta G_{et(1)}^\ddagger$) and k_{et} , respectively, were also calculated in this study for A-1 to A-7, B1 to B-7 and C-1 to C-7 (compounds 4-24) in accordance with the *Marcus* theory.

Keywords: Fullerenes; Hemoglobin A; Rehm-Weller equation; Free energy of electron transfer; Electron transfer properties; Activated free energies of electron transfer

INTRODUCTION

Hemoglobin A (HbA) is the main component of red blood cells and functions as an efficient oxygen carrier by reversibly binding oxygen at the heme group ferrous

ion. [1,2] The heme groups are embedded in each of the two *alpha*(α) and two *beta*(β) globin chains that form the molecule. In addition to regulating oxygen

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affinity, the globin structure serves to maintain the heme complex in its reduced state.[1] The binding, release and oxidation of oxygen occur at the heme group iron ion.[1] Changes at the heme group are accompanied by changes in the overall hemoglobin conformation.[1] The largest conformational change occurs at the β - β interface, which is at the closest approach in methemoglobin or oxyhemoglobin.[1,2] The oxidation-reduction (redox) studies of hemoglobin that were performed using spectroelectrochemistry (SEC) provided insight into the hemoglobin electron transfer process and, more specifically, into the heme group electronic factor and subunit interaction influences.[1] Bonaventura, Crumbliss and co-workers discovered that when a sixth ligand was bound to iron, the ligand could alter the redox behavior of hemoglobin in different ways while the electron density at the heme was varied [1-9]. Ligands with strong electron donor capabilities stabilized the ferric ion, shifting the formal redox potential in the negative direction.[1] The magnitude and direction of the formal redox potential shifts were found to be fine-tuned by the nature and concentration of the allosteric effectors (anions). The effect of the anions was attributed to the stabilization of one conformation relative to the other, which indirectly changed the electron density and steric environment at the heme iron.[1]

In 2008, the thermodynamics and kinetics of the following reaction: $\text{DeoxyHb-Fe}^{2+} \leftrightarrow \text{MetHb-Fe}^{3+}$, for human HbA and α - and β -fumarate crosslinked hemoglobins (α XL-HbA and β XL-HbA, respectively) were investigated using SEC by Dragan, Olsen, Moore and Fitch.[1]

Since the discovery of fullerenes (C_n), one of the main classes of carbon compounds, the unusual structures and physiochemical properties of these molecules have been discovered, and many

potential applications and physicochemical properties have been introduced. Up to now, various empty carbon fullerenes with different numbers "n" such as C_{60} , C_{70} , C_{76} , C_{82} and C_{86} , have been obtained. The chemical, physical and mechanical properties of empty and endohedral fullerenes have been the subject of many studies.[10-24] The compressive mechanical properties of fullerene molecules C_n ($n = 20, 60, 80, \text{ and } 180$) were investigated and discussed in detail using a quantum molecular dynamics (QMD) technique by Shen. [11,24] The unique stability of molecular allotropes such as C_{60} and C_{70} , was demonstrated in 1985. [10,11] This event led to the discovery of a whole new set of carbon-based substances, known as fullerenes.

After the discovery of C_{60} peapods by Luzzi *et al.* [12-17], the aligned structure of encapsulated molecules, due to the molecule-molecule and/or molecule-SWNT interactions, has been studied as a new type of hybrid material [14,15]. Zhang *et al.* [12] reported evidence for the latter interaction measuring the thermal stability of C_{60} peapods. [12-16]

The electrochemical properties of the C_{60} fullerene have been studied since the early 1990s, when these materials first became available in macroscopic quantities (for a review, see [14]). [13,14] In 1990, Haufler *et al.* [15] showed that CH_2Cl_2 electrochemically reduces C_{60} to C_{60}^{1-} and C_{60}^{2-} . In 1992, Echegoyen *et al.* [16] cathodically reduced C_{60} in six reversible one-electron steps for -0.97V vs. Fc/Fc^+ (Fc =ferrocene). This fact, along with the inability to perform anodic electrochemistry on fullerenes, matches the electronic structure of fullerenes: the LUMO of C_{60} can accept up to six electrons to form C_{60}^{6-} , but the position of the HOMO does not allow for hole-doping under the usual reported electrochemical conditions. In 1991, Bard *et al.* [17] first

reported on the irreversible electrochemical and structural reorganization of solid fullerenes in acetonitrile. Dunsch *et al.* [18] improved upon the experimental conditions by investigating highly organized C₆₀ films on HOPG, in an aqueous medium. The reduction of these films induces a morphological change; they re-structure into conductive nanoclusters of ~100 nm in diameter. [18,19]

Graph theory has been a useful tool in assessing the *QSAR* (Quantitative Structure Activity Relationship) and *QSPR* (Quantitative Structure Property Relationship). [25-36] Numerous studies in different areas have used topological indices (TI).[25-33] Any extrapolation of results from one compound to other compounds must take into account considerations based on a Quantitative Structural Analysis Relationship Study, which mostly depends on how close physical and chemical properties are of the compounds in question. It is important to use effective mathematical methods to make good correlations between several properties of chemicals. In 1993 and 1997, several complex applications of the indices were reported.[25-36] The numbers of carbon atoms at the structures of the fullerenes were utilized here.

This study elaborates upon the relationship between the number of carbon atoms and the free energies of electron transfer ($\Delta G_{et(l)}$) of fullerenes C_n (n=60, 70, 76, 82 and 86) with Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL- and β XL-[HbA], respectively, 1-3, on the basis of the oxidation potentials (^{ox}E) of the fullerenes, as assessed by applying the *Rehm-Weller* equation [37] to create C_n@[HbA], A-1 to A-5, C_n@ α XL-[HbA], B-1 to B-5 and C_n@ β XL-[HbA], C-1 to C-5. The results were extended to calculate the free energies of electron

transfer ($\Delta G_{et(l)}$) of other supramolecular complexes of Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL and β XL, respectively, 1-3 as a class of electron-transfer radicals, with fullerenes C₆₀ to C₃₀₀ C_n@X-[HbA] (HbA=Hemoglobin A; X= α - and β -Fumarate Crosslinked Hemoglobins (α XL & β XL)) 4-24 complexes, i.e.: C_n@[HbA] ; 4-8 & 19 & 20, C_n@ α XL-[HbA], 9-13 & 21 & 22 and C_n@ β XL-[HbA], 14-18 & 23 & 24 (supramolecular complexes 4-24). This study calculated the free energies of electron transfer ($\Delta G_{et(l)}$) of A-1 to A-7, B-1 to B-7 and C-1 to C-7. See Equations 1 to 19, Tables 1 to 3 and Figures 1 and 2.

In this study has also calculated the first activate free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(n)}^{\#}$ and k_{et} , respectively, as assessed using the *Marcus* theory and the equations on the basis of the first oxidation potential ($^{ox}E_1$) of fullerenes C_n (n=60, 70, 76, 82 and 86) for the predicted supramolecular complexes C_n@[HbA] ; **4-8 & 19 & 20**, C_n@ α XL-[HbA], **9-13 & 21 & 22** and C_n@ β XL-[HbA], **14-18 & 23 & 24** (supramolecular complexes **4-24**). See Equations 2 and 3, Tables 5 to 8 and Figure 3.

The Marcus theory is built on the traditional Arrhenius equation to determine the rates of chemical reactions in two methods. First, this theory provides a formula for the pre-exponential factor in the Arrhenius equation based on the electronic coupling between the initial and final state of the electron transfer reaction (i.e., the overlap of the electronic wave functions of the two states). Second, this theory provides a formula for the activation energy based on the reorganization energy parameter as well as the Gibbs free energy. The reorganization energy is defined as the amount of required energy to reorganize the system structure

from initial to final coordinates without changing the electronic state.

GRAPHING AND MATHEMATICAL METHOD

All graphs were generated using the *Microsoft Office Excel 2003* program. Using the number of carbon atoms contained within the C_n fullerenes, several valuable properties of the fullerenes can be calculated. The values were used to calculate the first free energies of electron transfer ($\Delta G_{et(1)}$), according to the *Rehm-Weller* equation for: $C_n@[HbA]$; **4-8** & **19** & **20**, $C_n@αXL-[HbA]$, **9-13** & **21** & **22** and $C_n@βXL-[HbA]$, **14-18** & **23** & **24** (supramolecular complexes **4-24**). This study calculated the free energies of electron transfer ($\Delta G_{et(1)}$) of **A-1** to **A-7**, **B-1** to **B-7** and **C-1** to **C-7**.

Both linear (MLR:Multiple Linear Regressions) and nonlinear (ANN:Artificial Neural Network) models were used in this study. Equations 1 and 4-18 were utilized to calculate the remaining values of $\Delta G_{et(1)}$ for complexes that have yet to be reported in the literature. Some of the other indices were examined, and the best results and equations for extending the physicochemical data were chosen. [31,36] The Rehm-Weller equation estimates the free energy change between an electron donor (D) and an acceptor (A) as [37]

$$\Delta G^\circ = e[E_D^\circ - E_A^\circ] - \Delta E^* + \omega_1 \quad (1)$$

where “ e ” is the unit electrical charge, E_D° and E_A° are the reduction potentials of the electron donor and acceptor, respectively, ΔE^* is the energy of the singlet or triplet excited state, and ω_1 is the work required to bring the donor and acceptor within the electron transfer (ET) distance. The work term in this expression can be considered to be ‘0’ in so far as an electrostatic

complex exists before the electron transfer.[37]

The Marcus theory of electron transfer implies rather weak (<0.05eV) electronic coupling between the initial (locally excited, LE) and final (electron transfer, CT) states and presumes that the transition state is close to the crossing point of the LE and CT terms. The value of the electron transfer rate constant k_{et} is controlled by the activation free energy ΔG_{et}^\ddagger , which is a function of the reorganization energy ($l/4$) and the electron transfer driving force ΔG_{et} :

$$\Delta G_{et}^\ddagger = (l/4)(1 + \Delta G_{et}/l)^2 \quad (2)$$

$$k_{et} = k_0 \exp(-\Delta G_{et}^\ddagger/RT) \quad (3)$$

The reorganization energy of organic molecules ranges from 0.1-0.3 eV. In this study, was used the minimum amount of reorganization energy.[43a-h].

RESULT AND DISCUSSION

Dragan, Olsen, Moore and Fitch have found that E_0 shifted positive for the α - and negative for the β -fumarate crosslinked hemoglobin compared to HbA for all experimental conditions investigated.[1] They have also reported that the formal redox potentials shifted positive with addition of nitrate and chloride ions for $\alpha XL-HbA$. [1] In their studies, they have suggested that the reduction of HbA is controlled by the driving force, ΔE_0 , whereas the reduction of $\alpha XL-HbA$ and $\beta XL-HbA$ occurs by a non-concerted mechanism controlled by structural features brought about by cross-linking.[1] The autoxidation reaction, conversion of oxygen-bound ferrous hemoglobin to ferric hemoglobin, was found independent of E_0 . $\alpha XL-HbA$ showed the highest autoxidation rate despite its positive shift in formal

redox potential as compared to HbA, followed by β -fumarate crosslinked hemoglobin, and by native hemoglobin.[1] These data suggest that the chemical

mechanism of oxygen dissociation and accessibility of water and oxygen radicals to heme site control autoxidation.[1]

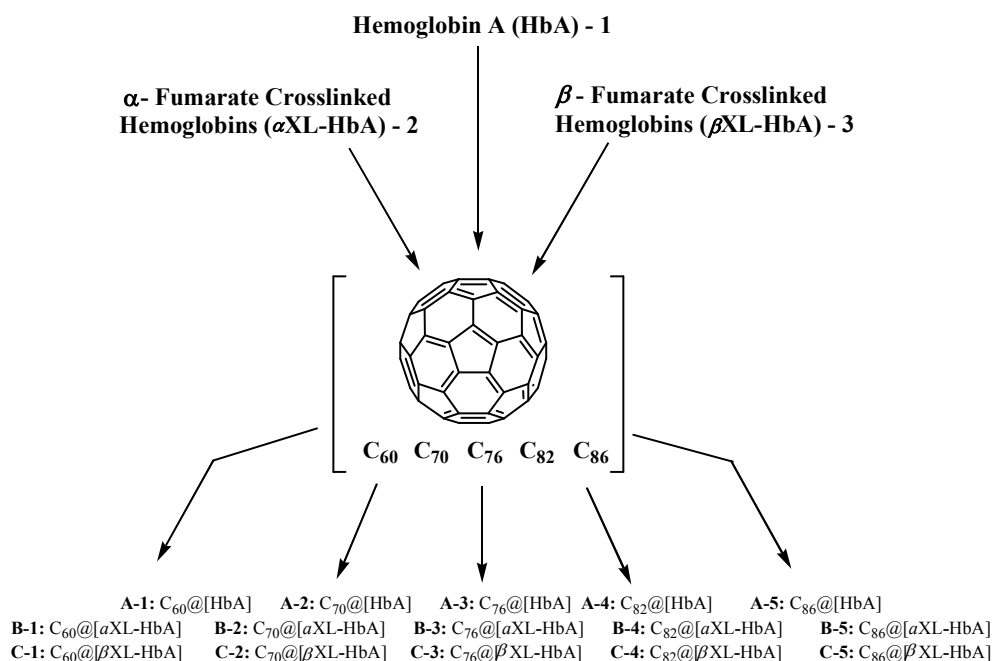


Fig. 1. The conjectured structures of Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL- and β XL-[HbA], respectively, 1-3 and fullerenes C_n ($n=60, 70, 76, 82$ and 86) which create $C_n@[HbA]$ A-1 to A-5, $C_n@[\alpha XL-HbA]$, B-1 to B-5 and $C_n@[\beta XL-HbA]$, C-1 to C-5. The different electrochemical conditions have shown in Table-7, which they were reported in Ref. [1].

Table 1. The values of the data coefficients of 4-8 (A-1 to A-5) and the values of the free energy of electron transfer (ΔG_{et}) in kcal mol⁻¹ between human Hemoglobin with C_n (as $C_n@[HbA]$) compounds A-6 and A-7) (forms 19 and 20) supramolecular complexes. The data of $\Delta G_{et(1)}$ are predicted by using Eq.-1 and Eq. 4 to Eq.-6

No.	Row	Formula of $C_n@[HbA]$	Supramolecular Complexes $C_n@[HbA]^2$				
			ΔG_{et}^1	ΔG_{et}^1 KCl 0.05 M	ΔG_{et}^1 KCl 0.2 M	ΔG_{et}^1 NaNO ₃ 0.05 M	ΔG_{et}^1 NaNO ₃ 0.20 M
4	A-1	C_{60}	24.77(24.77)	24.42 (24.42)	23.96(23.96)	24.35 (24.35)	24.21(24.21)
5	A-2	C_{70}	24.30(24.31)	23.96 (23.95)	23.49(23.48)	23.75(23.75)	23.89(23.88)
6	A-3	C_{76}	15.53 (15.54)	15.19 (15.18)	14.74(14.73)	15.13(15.13)	14.99(14.98)
7	A-4	C_{82}	13.46 (13.47)	13.12(13.11)	12.66(12.64)	13.05(13.05)	12.91(12.89)
8	A-5	C_{86}	13.68 (13.69)	13.35(13.34)	12.89(12.87)	13.28(13.28)	12.14(12.12)
19	A-6	C_{78}	14.08	13.73	13.28	13.69	13.58
20	A-7	C_{84}	13.71	13.37	12.89	13.29	12.83

¹ MOPS is equal to 0.05 mmol pH=7.1. Ru(NH₃)₆Cl₃⁻ 0.5 mmol. The experimental conditions were reported in the Ref.[1]

² The data of the free energy of electron transfer (ΔG_{et}) for $C_n@[HbA]$ compounds were not reported, previously.

Table 2. The values of the data coefficients of 9-13 (B-1 to B-5) and the values of the free energy of electron transfer (ΔG_{et}) in kcal mol⁻¹ between human Hemoglobin with C_n (as $C_n@αXL$ -[HbA]) compounds B-6 and B-7) (forms 21 and 22) supramolecular complexes. The data of $\Delta G_{et(1)}$ are predicted by using Eq.-1 and Eq. 4 to Eq.-6

No.	Row	Formula of $C_n@αXL$ -[HbA]	Supramolecular Complexes $C_n@αXL$ -[HbA] ²				
			ΔG_{et}^1	ΔG_{et}^1 KCl 0.05 M	ΔG_{et}^1 KCl 0.20 M	ΔG_{et}^1 NaNO ₃ 0.05 M	ΔG_{et}^1 NaNO ₃ 0.20 M
9	B-1	C_{50}	24.12(24.12)	23.94(23.94)	23.88(23.87)	23.94(23.94)	23.91(23.91)
10	B-2	C_{70}	23.66(23.66)	23.48(23.48)	23.42(23.41)	23.48(23.48)	23.44(23.45)
11	B-3	C_{75}	14.88(14.88)	14.71(14.71)	14.65(14.64)	14.70(14.71)	14.68(14.68)
12	B-4	C_{82}	12.81(12.82)	12.63(12.64)	12.58(12.57)	12.63(12.64)	12.60(12.61)
13	B-5	C_{85}	13.04(13.05)	12.86(12.87)	12.80(12.79)	12.86(12.87)	12.82(12.84)
21	B-6	C_{78}	13.43	13.26	13.20	13.25	13.23
22	B-7	C_{84}	13.07	12.89	12.83	12.89	12.85

¹ MOPS is equal to 0.05 mmol pH=7.1. Ru(NH₃)₆Cl₃⁻ 0.5 mmol. The experimental conditions were reported in the Ref.[1]

² The data of the free energy of electron transfer (ΔG_{et}) for $C_n@αXL$ -[HbA] compounds were not reported, previously.

Table-3: The values of the data coefficients of 14-18 (C-1 to C-5) and the values of the free energy of electron transfer (ΔG_{et}) in kcal mol⁻¹ between human Hemoglobin with C_n (as $C_n@βXL$ -[HbA]) compounds C-6 and C-7) (forms 23 and 24) supramolecular complexes. The data of $\Delta G_{et(1)}$ are predicted by using Eq.-1 and Eq. 4 to Eq.-6.

No.	Row	Formula of $C_n@βXL$ -[HbA]	Supramolecular Complexes $C_n@βXL$ -[HbA] ²				
			ΔG_{et}^1	ΔG_{et}^1 KCl 0.05 M	ΔG_{et}^1 KCl 0.20 M	ΔG_{et}^1 NaNO ₃ 0.05 M	ΔG_{et}^1 NaNO ₃ 0.20 M
14	C-1	C_{50}	25.09(25.09)	24.88(24.88)	24.84(24.84)	25.11(25.11)	25.11(25.11)
15	C-2	C_{70}	24.62(24.65)	24.41(24.42)	24.36(24.37)	24.64(24.65)	24.64(24.65)
16	C-3	C_{75}	15.86(15.87)	15.65(15.66)	15.60(15.61)	15.88(15.89)	15.88(15.89)
17	C-4	C_{82}	13.78(13.79)	13.57(13.58)	13.53(13.54)	13.80(13.81)	13.80(13.81)
18	C-5	C_{85}	14.03(14.02)	13.79(13.81)	13.76(13.77)	14.02(14.04)	14.02(14.04)
23	C-6	C_{78}	14.41	14.20	14.15	14.43	14.43
24	C-7	C_{84}	14.03	13.82	13.79	14.05	14.05

¹ MOPS is equal to 0.05 mmol pH=7.1. Ru(NH₃)₆Cl₃⁻ 0.5 mmol. The experimental conditions were reported in the Ref.[1]

² The data of the free energy of electron transfer (ΔG_{et}) for $C_n@βXL$ -[HbA] compounds were not reported, previously.

The experimental and literature values for the formal redox potential, E_0 (vs. NHE), and number of electrons transferred for the Ru(NH₃)₆ 3+/2+ couple were determined using conventional structure and thin-layer cyclic voltammetry (CV) and controlled potential coulometry (CPC) in various electrolyte / buffer systems by Fitch and co-workers.[1] In their studies, 3-(N-morpholino) propanesulfonic acid (MOPS), Ru(NH₃)₆Cl₃, myoglobin and

electrolytes, KCl and NaNO₃, were used.[1] The electrochemical condition results of Dragan, Olsen, Moore and Fitch are shown in the equation table.[1] Fitch and co-workers measured the potential against an Ag/AgCl reference electrode that was immersed in a background electrolyte solution.[1] A platinum wire and platinum were used as working electrodes.[1] When conventional CV was required for E_0 evaluation, the potentials

were measured against a saturated calomel electrode (SCE) using a platinum disc working electrode.[1]

The reported oxidation potentials ($^{Ox}E_1$) of fullerenes C_n ($n=60, 70, 76, 82$ and 86) are as follows: for C_{60} is, +1.21 Volt. The potential condition is irreversible and the related values were obtained by DPV pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s.[42] The $^{Ox}E_1$ (in Volt) for C_{70} is: +1.19.[42] The value of $^{Ox}E_1$ (in Volt) for C_{76} is: +0.81.[42] The value of $^{Ox}E_1$ for C_{82} is: +0.72 Volt.[42] The $^{Ox}E_1$ for C_{86} is: 0.73 Volt.[42] The oxidation potentials for C_{82} and C_{86} were reported for their major isomer.[42] The Values are in volts relative to ferrocene/ferrocenium couple. The conditions were: 0.1 M (n-Bu)₄NPF₆ in 1,2-dichlorobenzene; working electrode, Pt disk (1-mm diameter); counter electrode, Pt wire; reference electrode, Ag/0.01 M AgNO₃ and 0.1 M (n-Bu)₄NCIO₄ in CH₃CN. The CV reported scan rate was 20 mV/s.[42] C_{180} and C_{240} have not been prepared or isolated among the fullerenes which they have listed in Tables 1-6.

Tables 1-6 contain a summary of the data. They show the calculated values for 4-24 of the first free energies of electron transfer ($\Delta G_{et(1)}$ in kcal mol⁻¹) between Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL- and β XL-[HbA], respectively, 1-3 and fullerenes C_n ($n = 60, 70, 76, 82$ and 86) as $C_n@[HbA-X]$ (HbA=Hemoglobin A; X= α - and β -Fumarate Crosslinked Hemoglobins (α XL & β XL)) 4-24 complexes. These values were calculated using the *Rehm-Weller* equation (Eq.-1). The selected Hemoglobin A, α - and β -fumarate crosslinked hemoglobins, HbA, α XL- and β XL-[HbA] (1-3) were used to model the structural relationship between the number of carbon atoms in the

fullerenes and $\Delta G_{et(1)}$ (in kcal mol⁻¹). The data of $\Delta G_{et(1)}$ of the compounds A-1 to A-7, B-1 to B-7 and C-1 to C-7 (complexes 4-24) are reported in Tables 1-3. Figure-1 depicts the structures of the predicted complexes of create $C_n@[HbA]$, A-1 to A-5, $C_n@αXL-[HbA]$, B-1 to B-5 and $C_n@βXL-[HbA]$, C-1 to C-5.

Fig.-2 (graphs *a-c*) demonstrate the relationships between the number of carbon atoms of fullerenes “n” and the first free-energy of electron transfer ($\Delta G_{et(1)}$ in kcal mol⁻¹) of fullerenes ($n = 60, 70, 76, 82$ and 86) and 1-3 as $C_n@[HbA]$, A-1 to A-5, $C_n@αXL-[HbA]$, B-1 to B-5 and $C_n@βXL-[HbA]$, C-1 to C-5, complexes. Equations 4-6 correspond to Fig.-2 (graphs *a-c*) at the selected electrochemical conditions to determine the reduction potential of HbA 1, α XL-[HbA] 2 and β XL-[HbA] 3 (MOPS is equal to 0.05mmol, pH=7.1, Ru(NH₃)₆Cl₃ 0.5 mmol). These data was regressed with a fourth-order polynomial. The R-squared value (R²) for these graphs is equal to 1.00.

By using Equations 4-18 (see Table-7), it is possible to calculate the values of $\Delta G_{et(1)}$ of $C_n@[HbA]$, A-1 to A-7, $C_n@αXL-[HbA]$, B-1 to B-7 and $C_n@βXL-[HbA]$, C-1 to C-7 in the selected conditions (MOPS is equal to 0.05mmol, pH=7.1, Ru(NH₃)₆Cl₃ 0.5 mmol and the electrolytes KCl or NaNO₃). The $\Delta G_{et(1)}$ for $C_n@[HbA]$, $C_n@αXL-[HbA]$ and $C_n@βXL-[HbA]$ ($C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}$ and C_{84} .) are predicted by using Eq. 4-18 and the *Rehm-Weller* equation (see Tables 1-3 and 7).

By using Equations 1 and 7-9, it is possible to calculate the values of the first free energies of electron transfer ($\Delta G_{et(1)}$ in kcal mol⁻¹) of $C_n@[HbA]$, A-1 to A-7, $C_n@αXL-[HbA]$, B-1 to B-7 and $C_n@βXL-[HbA]$, C-1 to C-7 complexes in different electrochemical properties with Eq.4-6. Tables 1-3 have shown the

calculated values of $\Delta G_{et(1)}$ between HbA, α XL-[HbA] and β XL-[HbA] 1-3 and the C_n ($n=60, 72, 76, 82$ and 86) (as $C_n@[HbA]$, $C_n@[\alpha XL-[HbA]]$ and $C_n@[\beta XL-[HbA]]$) 9-13 and 21 & 23 supramolecular complexes in the selected conditions (MOPS is equal to 0.05mmol, pH=7.1, $Ru(NH_3)_6Cl_3$ 0.5 mmol and KCl 0.05M). The values of $\Delta G_{et(1)}$ for $C_n@[HbA]$ ($C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}$ and C_{84}) 9-13 and 21 & 23 are predicted by using equations 4-6 and the *Rehm-Weller* equation (see Tables 1-3 and 7). The values of R^2 for the graphs of the fourth-order polynomial equations 7-9 are equal to 1.00.

Equations 10-12, 13-15 and 16-18 have demonstrated the relationships between the number of carbon atoms of fullerenes "n" and the first free-energy of electron transfer ($\Delta G_{et(1)}$ in kcal mol⁻¹) of fullerenes ($n = 60, 70, 76, 82$ and 86) and 1-3 as $C_n@[HbA]$, A-1 to A-5, $C_n@[\alpha XL-[HbA]]$, B-1 to B-5 and $C_n@[\beta XL-[HbA]]$, C-1 to C-5, supramolecular complexes in different conditions. Equations 10-12, 13-15 and 16-18 correspond to the selected electrochemical conditions to determine the reduction potential of HbA 1, α XL-[HbA] 2 and β XL-[HbA] 3 (MOPS is equal to 0.05mmol, pH=7.1, $Ru(NH_3)_6Cl_3$ 0.5 mmol) and the different electrolyte concentrations of KCl and $NaNO_3$. These data was regressed with a fourth-order polynomial. The values of $\Delta G_{et(1)}$ for $C_n@[HbA]$ ($C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}$ and C_{84}) 14-18 and 23 & 24 are predicted by using equations 10-18 and the *Rehm-Weller* equation (see Tables 1-3 and 7). The values of R^2 for the graphs of the fourth-order polynomial equations 7-9 are equal to 1.00.

By utilizing these results (Eq. 4-18) and the *Rehm-Weller* equation, the first electron transfer energies of $\Delta G_{et(1)}$ of the complexes between selected class of

electron-transfer hemoglobin derivatives 1-3 with fullerenes ($C_{60}, C_{70}, C_{76}, C_{82}, C_{86}, C_{78}$ and C_{84}) were approximated (Tables 1 to 3 and 7). The calculated values of the first free electron transfer energies for selected $C_n@[HbA]$, $C_n@[\alpha XL-[HbA]]$ and $C_n@[\beta XL-[HbA]]$ ($n = 60, 70, 76, 82$ and 86 , compounds 4 to 24) in the *Rehm-Weller* equation and Eq. 4-18, are compared in Tables 1-3. There was good agreement between the calculated and the predicted values. In lieu of increasing the number of carbon atoms in the fullerene structure, the values of $\Delta G_{et(1)}$ were decreased. It seems that electron transfer increases as the electron population in the C_n structures increases. See Tables 1-3. It seems that these results are related to the HOMO and LUMO gap of the fullerenes. The Tables also shows that some of the first free electron transfer energies $\Delta G_{et(1)}$ values of $C_n@[HbA]$, $C_n@[\alpha XL-[HbA]]$ and $C_n@[\beta XL-[HbA]]$ are negative.

The *Marcus* theory is currently the dominant theory of electron transfer in chemistry. *Marcus* theory is so widely accepted because it makes surprising predictions about electron transfer rates that have been nonetheless supported experimentally over the last several decades. The most significant prediction is that the rate of electron transfer will increase as the electron transfer reaction becomes more exergonic, but only to a point. [43a-h]

Electron transfer (ET) is one of the most important chemical processes in nature, playing plays a central role in many biological, physical and chemical (both organic and inorganic) systems. Solid state electronics depends on the control of the ET in semiconductors, and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules and nanostructures. The other

reason to study electron transfer is that it is a very simple kind of chemical reaction and in understanding it, one can gain insight into other kinds of chemistry and biochemistry. After all, what is important is the chemistry of the transfer of electrons from one place to another. [43a-h]

The free energy of electron transfer ΔG_{et} is the difference between the reactants on the left and the products on the right, and $\Delta G_{et}^{\#}$, is the activation energy. The reorganization energy is the energy that it would take to force the reactants to have the same nuclear configuration as the products without permitting the electron transfer. If the entropy changes are ignored, the free energy becomes energy or potential energy. [43a-h]

In Tables 4-6 were shown the calculated values of the first free activation energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(1)}^{\#}$ and k_{et} by utilizing equations 2 and 3. Using Equations 2 and 3, it is possible to calculate the first activate free energies of electron transfer and kinetic rate constants of the electron transfers, $\Delta G_{et(1)}^{\#}$ and k_{et} , respectively, for 4-24 in accordance with Marcus theory.

The values of the first activated free energies of electron transfer, $\Delta G_{et(1)}^{\#}$ for 4-24, increase with increasing the $\Delta G_{et(n)}$ and the number of carbon atoms in the complexes, while the kinetic rate constants of the electron transfers $k_{et(1)}$, decrease with increasing $\Delta G_{et(1)}$ and $\Delta G_{et(1)}^{\#}$ for $C_n@[HbA]$; 4-8 & 19 & 20, $C_n@\alpha XL-[HbA]$, 9-13 & 21 & 22 and $C_n@\beta XL-[HbA]$, 14-18 & 23 & 24 (supramolecular complexes 4-24). See Tables 5-8 and Figure 3.

By using equation 1 (Rehm-Weller equation), equations 2 and 3 (Marcus theory) and Equations 4-18, the values of $\Delta G_{et(n)}$, $\Delta G_{et(1)}^{\#}$ and $k_{et(1)}$ were calculated for 4-24. The values of the number of carbon atoms (n) show a good relationship with the values of the first

free energies of electron transfer $\Delta G_{et(1)}$, $\Delta G_{et(1)}^{\#}$ and $k_{et(1)}$ in $C_n@[HbA]$; 4-8 & 19 & 20, $C_n@\alpha XL-[HbA]$, 9-13 & 21 & 22 and $C_n@\beta XL-[HbA]$, 14-18 & 23 & 24 (supramolecular complexes 4-24).

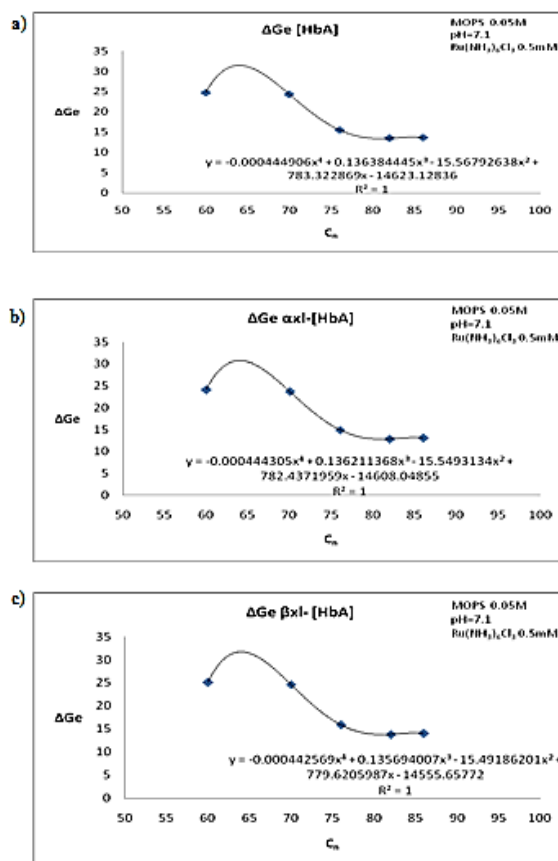


Fig. 2a-c. The relationship between the number “n” of carbon atoms in the fullerenes and the first free-energies of electron transfer ($\Delta G_{et(1)}$, in kcal mol⁻¹) of $C_n@[HbA]$, $C_n@\alpha XL-[HbA]$ and $C_n@\beta XL-[HbA]$ (n = 60, 70, 76, 82 and 86), compounds A-1 to A-5, in simple condition which they reported in Ref. [1]. (The related curves for B-1 to B-5 and C-1 to C-5 have similar structures to Fig-2 (A-1 to A-5) in different electrochemical reported which they have been reported in Ref.[1]. See Table-7)

Figure 3 shows the surfaces of the free energies of electron transfer $\Delta G_{et(1)}$ between 1-3 and fullerenes (C_{60} , C_{70} , C_{76} , C_{82} , C_{86} , C_{78} and C_{84}) in the structures of 4-24, calculated by Equations 1-18 and

shown in Tables 1-6. With the appropriate equations, it is possible to calculate the first free energies of electron transfer (ΔG_{et} in kcal.mol⁻¹), the first activated free energies of electron transfer and kinetic rate constants of the electron transfers, ΔG_{et}^\ddagger and $k_{et(1)}$, respectively, for C_n@[HbA] ; 4-8 & 19 & 20, C_n@ α XL-[HbA], 9-13 & 21 & 22 and C_n@ β XL-[HbA], 14-18 & 23 & 24 (supramolecular complexes 4-24), in close accordance with the results of *Marcus* theory.

The supramolecular complex structures which were discussed here, and the calculated values of $\Delta G_{et(1)}$, $\Delta G_{et(1)}^\ddagger$ and $k_{et(1)}$ corresponding to these supramolecular complexes were neither synthesized nor reported before.

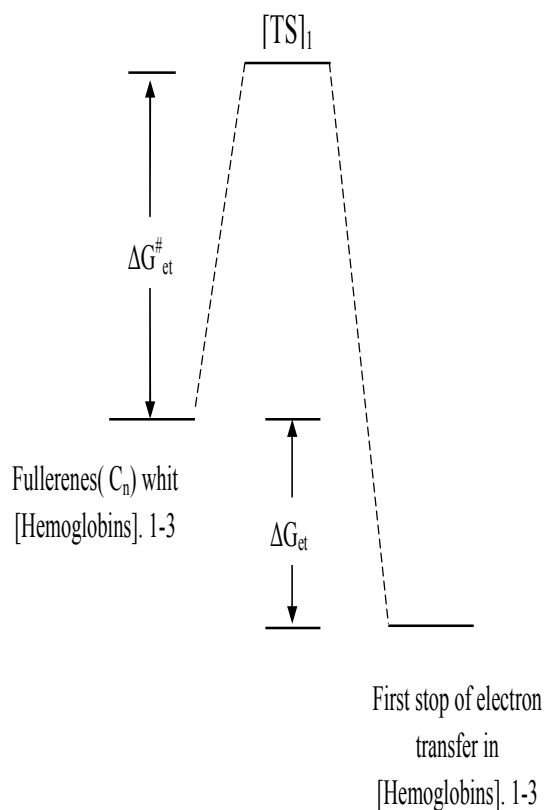


Fig. 3. The surfaces of the free energies of electron transfer $\Delta G_{et(n)}$ and $\Delta G_{et(n)}^\ddagger$ between 1-3 and the fullerenes in 4-24.

CONCLUSIONS

Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL and β XL, respectively, 1-3 and fullerenes have important electron-transfer properties as the most well-known ox/redox systems and biomolecular systems. The electrochemical data of Hemoglobin derivatives 1-3, i.e. C_n@[HbA] ; 4-8 & 19 & 20, C_n@ α XL-[HbA], 9-13 & 21 & 22 and C_n@ β XL-[HbA], 14-18 & 23 & 24 (supramolecular complexes 4-24) were reported here. These include the first free-energies of electron transfer ($\Delta G_{et(1)}$), calculated using the *Rehm-Weller* equation and $\Delta G_{et(1)}^\ddagger$ as well as $k_{et(1)}$ using equations of the *Marcus* theory for the supramolecular complexes 4-24. Using the number of carbon atoms (n), along with the equations of the model, one can derive sound structural relationships between the aforementioned physicochemical data. These equations allow one to calculate $\Delta G_{et(1)}$, $\Delta G_{et(1)}^\ddagger$ and $k_{et(1)}$ for Hemoglobin A, α - and β -Fumarate Crosslinked Hemoglobins, HbA, α XL- and β XL-[HbA], respectively, 1-3 as 4-8 & 19, 20, 9-13 & 21, 23 and 14-18 & 23, 24 (supramolecular complexes 4-24) of the fullerenes (C₆₀, C₇₀, C₇₆, C₈₂, C₈₆, C₇₈ and C₈₄). The novel supramolecular complexes discussed have neither been synthesized nor reported previously.

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Table 4. The values of the free activation energies of electron transfer ($\Delta G_{et}^{\#1}$) and the electron transfer rate constants (k_{et}) of human Hemoglobin with C_n (as $C_n@$ [HbA] compounds (A-1 to A-7) supramolecular complexes

No.	Row	C_n	$C_n@$ [HbA]		$C_n@$ [HbA] KCl 0.05M		$C_n@$ [HbA] KCl 0.2M		$C_n@$ [HbA] NaNO ₂ 0.05M		$C_n@$ [HbA] NaNO ₂ 0.20M	
			$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}
4	A-1	C ₆₀	31.32	6.19×10^{11}	30.68	1.83×10^{10}	29.84	7.47×10^{10}	30.55	2.27×10^{10}	30.30	3.49×10^{10}
5	A-2	C ₇₀	30.48	2.57×10^{10}	29.83	7.70×10^{10}	29.00	3.08×10^9	29.47	1.41×10^9	29.70	9.52×10^{10}
6	A-3	C ₇₆	16.62	3.74	16.15	8.22	15.56	22.26	16.08	9.40	15.88	13.11
7	A-4	C ₈₂	13.95	3.42	13.53	189.97	12.98	1750	13.45	796.01	13.25	1110
8	A-5	C ₈₆	14.21	216.33	13.81	429.99	13.25	1100	13.73	496.081	12.35	5090
19	A-5	C ₇₈	14.72	92.83	14.28	194.78	13.73	496.81	14.23	211.84	14.09	266.68
20	A-7	C ₈₄	14.26	203.14	13.84	412.58	13.25	1100	13.74	486.68	13.18	1240

¹ MOPS is equal to 0.05 mmol pH=7.1. Ru(NH₃)₆Cl₃ 0.5 mmol. The experimental conditions were reported in the Ref.[1]

Table 5. The values of the free activation energies of electron transfer ($\Delta G_{et}^{\#1}$) and the electron transfer rate constants (k_{et}) of α -Fumarate Crosslinked Hemoglobins with C_n (as $C_n@$ [α 1-HbA] compounds (B-1 to B-7) supramolecular complexes

No.	Row	C_n	$C_n@$ [\alpha1-HbA]		$C_n@$ [\alpha1-HbA] KCl 0.05M		$C_n@$ [\alpha1-HbA] KCl 0.2M		$C_n@$ [\alpha1-HbA] NaNO ₂ 0.05M		$C_n@$ [\alpha1-HbA] NaNO ₂ 0.20M	
			$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}
9	B-1	C ₆₀	30.13	4.59×10^{10}	29.81	7.94×10^{10}	29.70	9.52×10^{10}	29.81	7.93×10^{10}	29.76	8.69×10^{10}
10	B-2	C ₇₀	29.31	1.85×10^9	28.99	3.18×10^{10}	28.88	3.80×10^9	28.99	3.18×10^9	28.91	3.58×10^9
11	B-3	C ₇₆	15.75	16.36	15.53	23.77	15.45	27.11	15.51	24.30	15.49	25.39
12	B-4	C ₈₂	13.16	1290	12.94	1860	12.88	2050	12.94	1860	12.91	1970
13	B-5	C ₈₆	13.43	812.41	13.22	1170	13.15	1320	13.22	1170	13.17	1270
21	B-5	C ₇₈	13.91	364.36	13.70	517.70	13.63	585.65	13.69	528.46	13.66	530.65
22	B-7	C ₈₄	13.47	764.19	13.25	1100	13.18	1240	13.25	1100	13.17	1270

¹ MOPS is equal to 0.05 mmol pH=7.1. Ru(NH₃)₆Cl₃ 0.5 mmol. The experimental conditions were reported in the Ref.[1]

Table 6. The values of the free activation energies of electron transfer ($\Delta G_{et}^{\#1}$) and the electron transfer rate constants (k_{et}) of β -Fumarate Crosslinked Hemoglobins with C_n (as $C_n@[\beta XL-HbA]$) compounds (C-1 to C-7) supramolecular complexes

No	Row	C_n	$C_n@[\beta XL-HbA]$		$C_n@[\beta XL-HbA]$ KCl 0.05M		$C_n@[\beta XL-HbA]$ KCl 0.2M		$C_n@[\beta XL-HbA]$ NaN ₃ 0.05M		$C_n@[\beta XL-HbA]$ NaN ₃ 0.20M	
			$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}	$\Delta G_{et}^{\#1}$	k_{et}
14	C-1	C ₆₀	31.91	2.28×10 ⁻¹¹	31.52	4.39×10 ⁻¹¹	31.45	7.98×10 ⁻¹¹	31.95	2.14×10 ⁻¹¹	31.95	2.14×10 ⁻¹¹
15	C-2	C ₇₀	31.04	9.86×10 ⁻¹¹	30.66	1.89×10 ⁻¹⁰	30.59	2.13×10 ⁻¹⁰	31.08	9.27×10 ⁻¹¹	31.10	8.98×10 ⁻¹¹
16	C-3	C ₈₂	17.05	1.80	16.77	2.91	16.71	3.19	17.08	1.72	17.09	1.68
17	C-4	C ₈₂	14.34	175.33	14.09	266.68	14.03	295.99	14.38	164.59	14.37	168.10
18	C-5	C ₈₂	14.65	103.27	14.38	164.59	14.35	171.68	14.66	103.27	14.64	105.49
23	C-5	C ₇₈	15.14	45.69	14.87	71.82	14.81	79.93	15.16	43.75	15.16	43.75
24	C-7	C ₈₄	14.65	103.27	14.39	161.16	14.35	171.68	14.68	98.96	14.68	98.96

Table 7. Fourth order polynomial equations 4-18 that indicate the relationship between the number of carbon atoms “n” in the fullerenes and the first free energies of electron transfer ($\Delta G_{et(n)}$, in kcal mol⁻¹) of $C_n@[HbA]$, $C_n@\alpha XL-[HbA]$ and $C_n@ \beta XL-[HbA]$ (n = 60, 70, 76, 82 and 86), compounds A-1 to A-7, B-1 to B-7 and C-1 to C-7 in accordance with the reported experimental conditions of Ref. [1]

Eq. No./Hemoglobin	a	b	c	d	e	Exp. Conditions ¹
4 [HbA]	-0.000444305	0.136211368	-15.5493134	782.4371959	-14608.04855	MOES 0.05M
5 $\alpha XL-[HbA]$	-0.000444906	0.136384445	-15.56792638	783.322869	-14623.12836	$pH=7.1$ $R_w(NH_3)Cl_0.5m$
6 $\beta XL-[HbA]$	-0.000442569	0.135694007	-15.49186201	779.6205987	-14555.65772	MOES 0.05M
7 [HbA]	-0.000444305	0.136211368	-15.5493134	782.4371959	-14607.74855	MOES 0.05M
8 $\alpha XL-[HbA]$	-0.000444305	0.136211368	-15.5493134	782.4371959	-14608.22855	$pH=7.1$ $R_w(NH_3)Cl_0.5m$
9 $\beta XL-[HbA]$	-0.000442569	0.135694007	-15.49186201	779.6205987	-14555.86772	$R_w(NH_3)Cl_0.5m$ KCl 0.05M
10 [HbA]	-0.000430416	0.131999563	-15.07307729	758.6552098	-14165.59939	MOES 0.05M
11 $\alpha XL-[HbA]$	-0.000444305	0.136211368	-15.5493134	782.4371959	-14608.22855	$pH=7.1$ $R_w(NH_3)Cl_0.5m$
12 $\beta XL-[HbA]$	-0.000442569	0.135694007	-15.49186201	779.6205987	-14555.63772	$R_w(NH_3)Cl_0.5m$ NaN ₃ 0.05M
13 [HbA]	-0.000514818	0.156696144	-17.77194481	889.1532953	-16520.31682	MOES 0.05M
14 $\alpha XL-[HbA]$	-0.000442569	0.135694007	-15.49186201	779.6205987	-14556.83772	$pH=7.1$ $R_w(NH_3)Cl_0.5m$
15 $\beta XL-[HbA]$	-0.000442569	0.135694007	-15.49186201	779.6205987	-14555.63772	$R_w(NH_3)Cl_0.5m$ NaN ₃ 0.2M
16 [HbA]	-0.000441701	0.135430118	-15.46194882	778.1230709	-14528.87355	MOES 0.05M
17 $\alpha XL-[HbA]$	-0.000444906	0.136384445	-15.56792638	783.322869	-14624.02836	$pH=7.1$ $R_w(NH_3)Cl_0.5m$
18 $\beta XL-[HbA]$	-0.000443437	0.135947480	-15.5194002	780.9396681	-14579.41439	$R_w(NH_3)Cl_0.5m$ KCl 0.2M

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