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Short Communication

DETERMINATION OF BINDING PARAMETERS OF 2-(FERROCENYLMETHYL-AMINO)BENZONITRILE AND 3-(FERROCENYLMETHYLAMINO)BENZO-NITRILE WITH 1,1-DIPHENYL-2-PICRYLHYDRAZYL FREE RADICAL

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ABSTRACT

Spectrophotometric techniques based assay were developed for the determination of binding parameters like binding constant and binding free energy of two potential antioxidants ferrocene derivatives: 2-(ferrocenylmethylamino)benzonitrile (2FMAB), 3-(ferrocenylmethyl-amino)benzonitrile (3FMAB), and a standard ascorbic acid (AA) with 1,1-diphenyl-2-picrylhydrazyl radicals (DPPH). Obtained resultants indicated that the adduct 3FMBA-DPPH shows highest binding constant and highest binding free energy (2.28×10^{5} M^{-1}) and (-30.59 $KJmol^{-1}$) respectively. Binding free energy of 3FMAB-DPPH is almost three times greater than that of the adduct 2FMAB-DPPH (-10.47 $KJmol^{-1}$) and also is greater than the adduct formed between the standard antioxidant ascorbic acid and 1,1-diphenyl-2-picrylhydrazyl radicals (AA-DPPH) (-19.29 $KJmol^{-1}$).

Key word : ferrocene derivatives, DPPH, binding parameters, binding free energy, binding constant.

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1. INTRODUCTION

Ferrocene derivatives containing amine groups can be considered as potential antioxidants, they attracted and keep attracting the attention of many researchers due to their stability and biological activity [1,2]. The antioxidant activity of this type of derivatives was first studied in

the late 1950s by Acton and Silverstein [3] whom report the synthesis and antioxidant activity of a series of N-substituted ferrocenecarboxyamides and ferrocenylamine derivatives. Zhang and Liu [4] also reported the antioxidant activity of ferrocenylhydrazones and found that they exhibit an interesting antioxidant activity. After that many researchers synthesized and studied the antioxidant activities of many ferrocene derivatives.

Although interaction of antioxidant standards and potential antioxidants compounds with superoxide anion radicals has been studied by a few researchers [5-8], their interaction with DPPH has not been reported yet.

In this present study we report the synthesis of 2-(ferrocenylmethylamino)benzonitrile and 3-(ferrocenylmethylamino)benzonitrile and the determination of their binding parameters with 1,1-diphenyl-2-picrylhydrazyl radicals using spectrophotometric method.

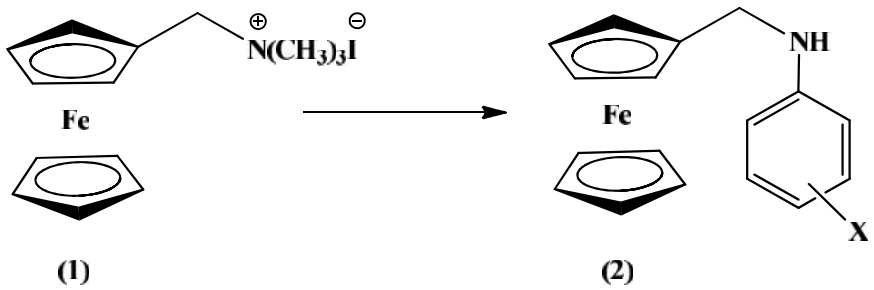
2. MATERIALS AND METHODS

Chemicals and reagents

Acetonitrile (ACN) (HPLC-grade from Sigma-Aldrich) was used as solvent without further purification, 1,1-diphenyl-2-picrylhydrazyl (DPPH) (99%) and ascorbic acid (99.7%) from Alfa Aesar. All other reagents used are (analytical grade).

2.1. Synthesis

2-(ferrocenylmethylamino)benzonitrile and 3-(ferrocenylmethylamino)benzonitrile were synthesized as described previously [9] cleanly and in high yield from the reaction of the well-known quaternary salt ferrocenylmethyltrimethylammonium iodide [10] (1) and 2- and 3-aminobenzonitrile respectively, scheme 1. All compounds gave analytical and spectroscopic data in accordance with the proposed structures.



Scheme 1. Synthesis of (ferrocenylmethylamino)benzonitrile, 2FMAB: X = 2-CN, 3FMAB: X = 3-CN,

3. RESULTS AND DISCUSSION

3.1. Spectrophotometric studies of 2FMAB –DPPH and 3FMAB –DPPH interaction

Diminution of absorbance of the electronic spectra of DPPH in the presence of 2FMAB and 3FMAB was used for the calculation of the binding constant and the binding free energy of the adducts 2FMAB-DPPH and 3FMAB-DPPH. The effect of different concentration of 2FMAB and 3FMAB on the electronic absorption spectrum of a 10^{-4} M solution of DPPH in acetonitrile is shown in figure 1. It was observed that DPPH had one strong absorption peak at 518 nm. After interaction with increasing amount of 2FMAB and 3FMAB, this peak decreased gradually. The concentrations of 2FMAB and 3FMAB were chosen based on the optimal response in the electronic absorption spectrum the electronic absorption spectrum.

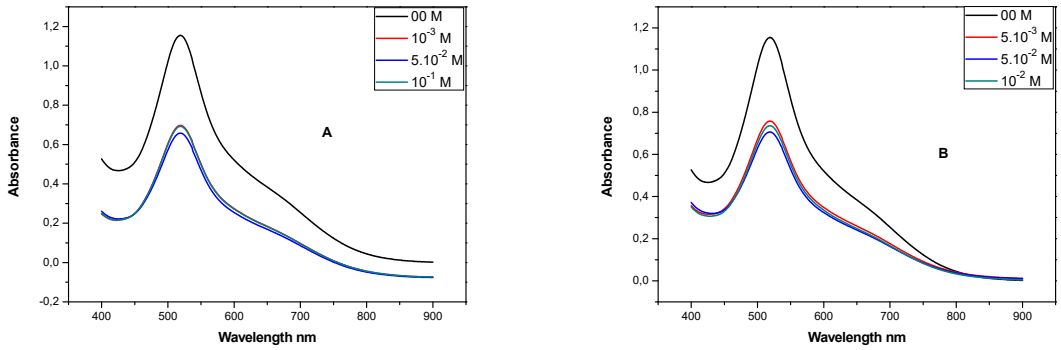


Fig.1. Electronic absorption spectra of 0.1 mM DPPH interaction with 2FMAB (A) and 3FMAB (B) in ACN

3.2. Binding constant

The binding constant and binding free energy were calculated based upon the decrease in absorbance using the equation of Benesi-Hildebrand[11] (1),

$$\frac{A_0}{A-A_0} = \frac{£_0}{£-£_0} + \frac{£_0}{£-£_0}\frac{1}{KC} \quad (1)$$

Were A_0 and A are absorbances of the free and bound ferrocene derivatives, ε and ε_0 are their absorption coefficients respectively, C is the concentration of potential antioxidant ferrocene derivatives, K is the binding constant.

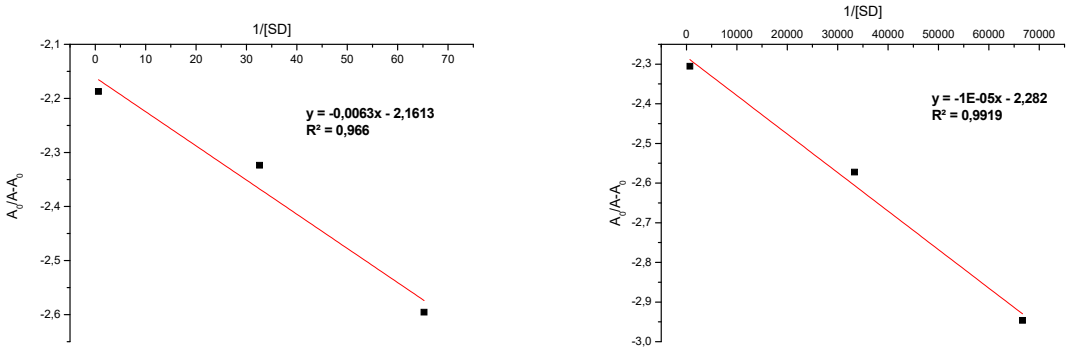


Fig.2. plot of 1/C versus $A_0/A-A_0$

The slope to intercept ratio of the plot between A/A_0-A versus 1/C yielded the binding constants, results are summarised in Table 1. Interaction parameters of the standard ascorbic acid with DPPH were also determined (data are not presented). The moderate binding constants of DPPH-AA and DPPH-2FMAB are indicative of electrostatic interaction, however higher values of binding constants of DPPH-3FMAB are indicative of chemical interaction. The negative values of the Gibbs energy change signify the spontaneity of the interactions.

Table 1. Binding constants and binding free energy values

Compound	Equation	R^2	K (l/mol)	ΔG(KJ/mol)
DPPH-AA	y = -0.0012x – 2.92	0.997	2.43×10^3	-19.29
DPPH-2FMAB	y = -0.0063x – 2.1613	0.967	3.43×10^2	-10.47
DPPH-3FMAB	$y = -10^{-5}x – 2.282$	0.992	2.28×10^5	-30.59

4. CONCLUSION

Two ferrocene derivatives 2-(ferrocenylmethylamino)benzonitrile (2FMAB) and 3-(ferrocenylmethylamino)benzonitrile (3FMAB) were successfully synthesised and their binding parameters with DPPH radical were determined using spectrophotometrical technics. The results indicated chemical interaction of DPPH radical with 3FMAB and electrostatic interaction of 2FMAB and Ascorbic acid with DPPH as the dominant mode. spectrophotometrical data allowed the estimation of binding parameters like binding constant, and binding free energy.

5. ACKNOWLEDGMENT

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