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Enantioanalysis of R-deprenyl based on its molecular interaction with C_{70} fullerenes

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ABSTRACT

Two enantioselective, potentiometric membrane electrodes based on [5,6]fullerene-C_{70} (**1**) and diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate (**2**) immobilized in carbon paste, were designed for the enantioanalysis of R-deprenyl. The electrodes exhibited near-Nernstian slopes: 57.90 (**1**) and 59.00 mV/decade of concentration (**2**), respectively with low limits of detection 5.9×10^{-11} (**1**) and 9.6×10^{-11} mol/L (**2**), respectively. The linear concentration ranges are between 10^{-10} and 10^{-4} mol/L (**1**) and between 10^{-9} and 10^{-4} mol/L (**2**), respectively. The different characteristics involved in the molecular interaction between R-deprenyl and C_{70} fullerenes were explained, namely (i) the stability of each molecule and (ii) the explanation of the molecular mechanism of interaction, using restricted Hartree–Fock theory, 3-21G(*) RHF-basis set. Furthermore, two intermolecular forces of interactions confer the stability of the electrodes; electrostatic interaction and moderate hydrogen bond interaction. Stability and feasibility of all the generated structures involved in this analysis were supported by their respective fundamental frequencies and energy minima.

R-deprenyl can be recovered with average recoveries higher than 99.10% (RSD < 0.03%) from synthetic mixtures between R- and S-deprenyl. The high selectivity and enantioselectivity made possible the enantioanalysis of R-deprenyl in its pharmaceutical formulations.

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1. Introduction

Enantioanalysis of pharmaceutical compounds with a chiral moiety became very important because different enantiomers of the same chiral substance may have different pathways in the body [1]. Deprenyl (Dep) is an irreversible inhibitor of monoamine oxidase enzyme (MAO) [2,3]. R-deprenyl (R-dep) selectively inhibits MAO type B while S-deprenyl (S-dep) selectively inhibits MAO type A [4]. The "A" form is responsible for breaking down the neurotransmitters serotonin, adrenalin and noradrenalin, while the "B" form is breaking down the dopamine. R-deprenyl and its metabolites also inhibit the monoamine transporters in the brain [5–7]. Therefore, it is a need to reliable enantioanalyse R-deprenyl.

To date, the following methods were proposed for the analysis and enantioanalysis of deprenyl: capillary electrophoresis [8–12], liquid chromatography [13], gas chromatography [14,15] and planar chromatography [16]. Capillary electrophoresis was the most reliable method proposed. Unfortunately, using capillary electrophoresis is not possible to get high sensitivity. Therefore, we proposed for the enantioanalysis of R-deprenyl two enantioselective, potentiometric membrane electrodes (EPME). The chiral selectors used for the design of the electrodes are C_{70} fullerenes. The reason to select these chiral selectors was to improve the sensitivity, selectivity and enantioselectivity of the electrodes, to decrease their limit of detection, and to enlarge the working concentration range. Furthermore, by immobilization of fullerenes in carbon paste, one can obtain biocompatible electrodes which can be used for *in vivo* enantioanalysis of R-deprenyl.

Restricted Hartree–Fock (RHF) calculations were performed using 3-21G(*) basis set, directed towards the understanding of the mechanism of intermolecular interaction between R-deprenyl and C_{70} fullerenes. Indeed, the modeling of molecular interaction is useful for the enantioanalysis.

2. Experimental

2.1. Reagents and materials

[5,6]Fullerene-C_{70} (**1**), diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate (**2**) and paraffin oil were purchased from Fluka (Buchs, Switzerland). R- and S-deprenyl (R- and S-dep) were purchased from Sigma–Aldrich (USA). Graphite powder (1–2 μm) was purchased from Aldrich (Milwaukee, WI, USA). Phosphate

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buffer (pH 5.82) was purchased from Merck (Darmstadt, Germany). Deionized water was obtained using the Modulab System (Continental Water Systems, San Antonio, TX, USA).

Stock R- and S-deprenyl solutions were freshly prepared in a phosphate buffer of pH 5.82 by serial dilutions. Buffer and standard solutions were prepared using deionized water. All chemicals were of analytical reagent grade.

Lentogesic tablets (65 mg deprenyl per tablet) were obtained from Adcoc Ingram Limited (Johannesburg, South Africa).

2.2. Electrode design

Paraffin oil and graphite powder were mixed in a ratio 1:4 (w/w) to form the plain carbon paste. The modified carbon pastes were prepared by impregnating 100 μL of 10^{-3} mol/L of each fullerene (**1** and **2**) in 0.1 g of the plain carbon paste. A certain amount of carbon paste, free of fullerene, was filled in a plastic pipette peak, leaving 3–4 mm in the top to be filled with the modified carbon paste containing the chiral selector. The diameter of two EPMEs was 3 mm. Electric contact was obtained by inserting silver wires into the carbon matrix. The internal solution was 0.1 mol/L KCl.

The electrode surface was gently rubbed on fine abrasive paper to produce a flat surface. The surface of the electrode was wetted with deionized water, refreshed with modified carbon paste and then polished with an alumina paper (polished strips 30144-011, Orion) before use for the analysis.

2.3. Apparatus

A 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 12 and software (Eco Chemie Version 4.9) was used for all potentiometric measurements. An Ag/AgCl (0.1 mol/L KCl) electrode was used as reference electrode in the cell.

2.4. Recommended procedure

2.4.1. Direct potentiometry

The potentiometric technique was used for potential determination of each standard solutions 10^{-10} to 10^{-3} mol/L. The electrode was placed into stirred standard solutions and graphs of *E* (mV) versus pR-deprenyl were plotted. The unknown concentrations were determined from the calibration graphs.

2.4.2. Content uniform assay of deprenyl tablets

Each of the ten tablets were placed into 100 mL calibrated flask, dissolved and diluted to the mark using a phosphate buffer (pH 5.85):deionized water 1:1. The unknown concentration of R-deprenyl was determined using the direct potentiometric method.

2.5. Computational method

The structures [5,6]fullerene-C_{70} (**1**), diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate (**2**), N-protonated R-deprenyl (R-dep) (**3**), complex between R-dep and [5,6]fullerene-C_{70} (**4**), and complex between R-dep and diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxyate (**5**), were generated to propose the mechanism of interaction between R-dep and fullerene as chiral selector.

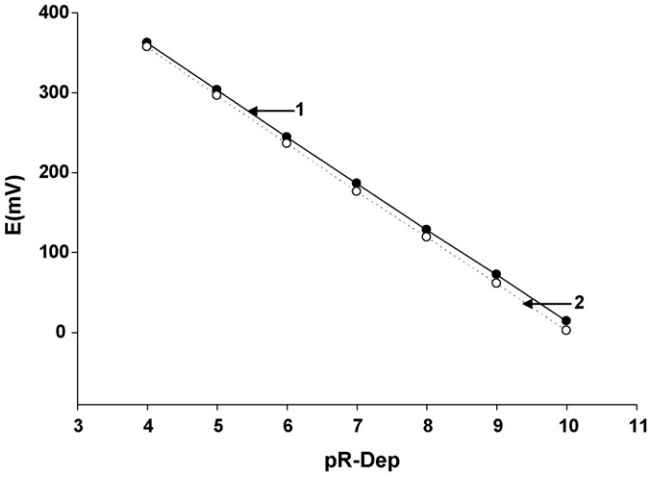

Fig. 1. Calibration graphs of [5,6]fullerene-C_{70} (**1**) and diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate (**2**) based enantioselective potentiometric electrodes (pR-dep = $-\log[C_{R\text{-dep}}]$).

The lower energy conformational electronic structures of all the compounds **1**–**5** were obtained using ab initio theory. Though, molecular calculations started with the fully optimized, semiempirical PM3 level of theory, followed by the minimal STO-3G basis set restricted Hartree–Fock model. The resulting wavefunction, Hessian matrix and the geometry of molecules obtained were used to perform a final calculation with the split-valence basis set 3-21G(*) RHF model. The asterisk means that "d" polarization functions were added for carbon, oxygen and nitrogen atoms.

To obtain the detain picture of chiral interaction, the following physicochemical parameters were used: total energy, highest occupied MO (HOMO), lowest unoccupied MO (LUMO), atomic charge, intermolecular distance of interaction, bond length, hardness (η) and dipole moment (μ). Fundamental frequencies at the semiempirical level (PM3) of all the molecules and complexes were calculated.

Computational calculations were carried out using a Pentium 4 (3.2 GHz) based computer. The software utilized was Spartan'04 Windows [17] and CorelDRAW 12.

3. Results and discussion

3.1. Response characteristics of the enantioselective, potentiometric electrodes

The potentiometric electrodes based on **1** and **2** exhibited near-Nernstian response only for R-deprenyl. The calibration graphs are shown in Fig. 1. No response was obtained for S-deprenyl (The average slope was 3 mV/decade of concentration). Accordingly, they cannot be used for the enantioanalysis of S-deprenyl.

The response characteristics obtained for R-deprenyl are summarized in Table 1. Utilization of fullerenes as chiral selectors in the

Table 1
Response characteristics of the enantioselective, potentiometric electrodes based on C_{70} fullerenes[a].

Electrode based on	Slope (mV/decade of concentration)	Intercept, *E* (mV)	Linear concentration range (mol/L)	Detection limit (mol/L)
1	57.90	592.50	10^{-10} to 10^{-4}	5.9×10^{-11}
2	59.00	591.10	10^{-9} to 10^{-4}	9.6×10^{-11}

[a] All measurements were made at room temperature; all values are the average of 10 determinations.

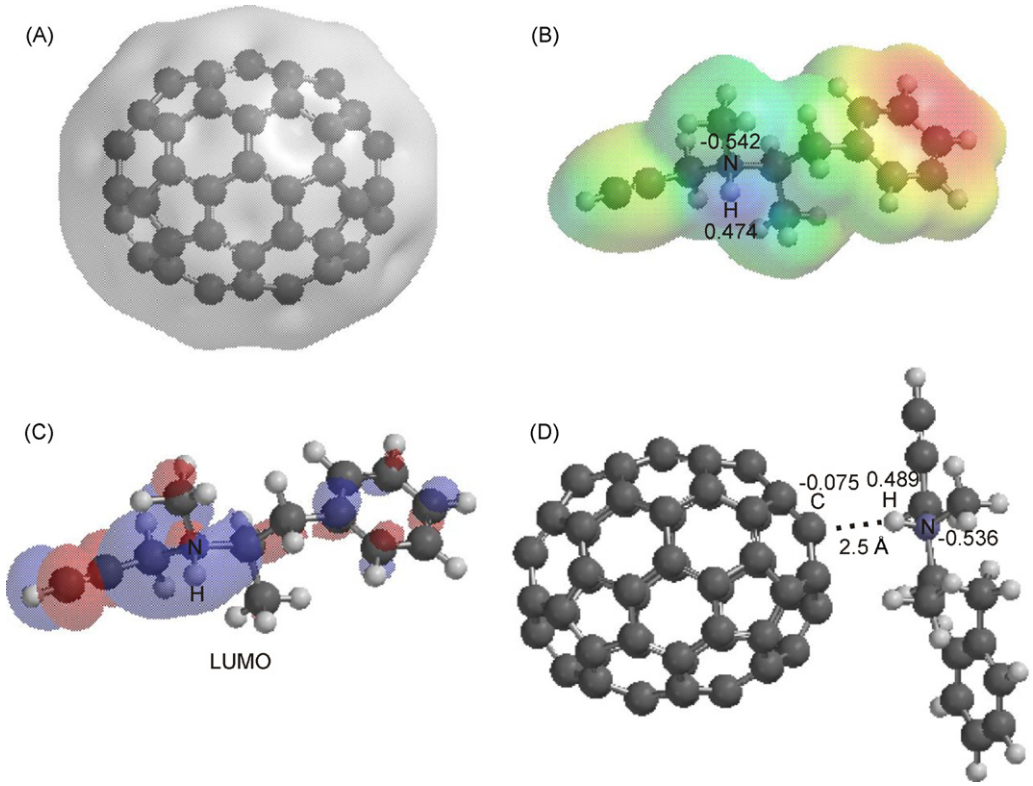

Fig. 2. (A) Electronic density of [5,6]fullerene-C_{70} presenting its overall molecular size and shape. (B) The electronic density encoded with electrostatic potential map of N-protonated R-deprenyl, blue is electropositive region and red is electronegative region; significant charges are labelled. (C) The lowest unoccupied molecular orbital of N-protonated R-deprenyl. (D) Electronic structure of the complex formed between [5,6]fullerene-C_{70} and N-protonated R-deprenyl, showing distance of interaction; significant charges are labelled. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

design of the enantioselective, potentiometric electrodes favorised the increasing of sensitivities and of the working concentration ranges, and the decreasing of the detection limits. Also, the values of the slopes obtained were closed with the Nernstian value. The limits of detection were determined from the calibration equations using statistics approach for data processing (linear least-square plots). The low values obtained for the limits of detection are due to utilization of KCl 0.1 mol/L solution as internal solution in the electrode design; this proving the statements of Sokalski et al. [18]. The advantage of using C_{70} fullerenes as chiral selectors over maltodextrines [19] is the significant improvement of the sensitivity of the electrodes; the slopes obtained by using the sensors proposed in this paper being higher than those obtained by using EPME based on maltodextrines.

The response times were 1 min when [5,6]fullerene-C_{70} based electrode was used and 30 s when diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate based electrode was used. The response obtained for two electrodes shown good stability and reproducibility for tests performed for more than 1 month (RSD < 0.1%).

3.1.1. Mechanism of potential development

The explanation for the potential development is based on the correlation done between the experimental results and computational calculations.

The lower energy conformation, electronic and molecular properties were calculated for the chiral selectors **1** and **2** individually, and along with R-dep as the complexes **4** and **5**, respectively. Electronic structure as well as physicochemical properties of free N-protonated R-deprenyl (**3**) is also calculated. The computer generated lower energy electronic structures are presented in Figs. 2 and 3.

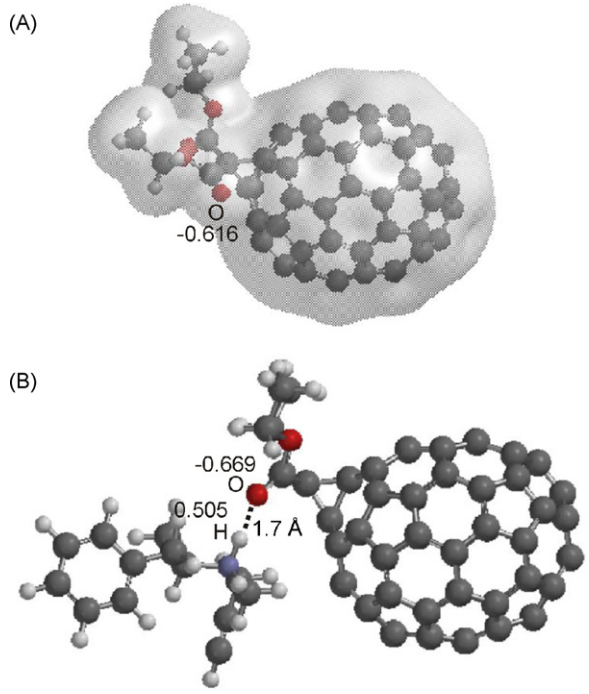

Fig. 3. (A) The electronic density surface of diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate where the atomic charge of oxygen is labelled. (B) Electronic and molecular structure of the complex formed between diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate and N-protonated R-deprenyl, indicating intermolecular distance of interaction and significant charges.

Table 2
Values of the physicochemical properties of the compounds involved in the complex formation between fullerene and R-deprenyl.

Compound	1	2	3	4	5
Total energy[a]	−2635.63650	−3202.82157	−553.862274	−3189.47604	−3756.71218
HOMO[b]	−7.97	−7.57	−12.04	−9.86	−9.53
LUMO[b]	−0.84	−0.61	0.64	−3.02	−2.76
Hardness[b]	3.57	3.48	6.34	3.42	3.39
Dipole moment[c]	0.00	5.41	7.23	16.66	13.78

[a] Hartrees.
[b] Electron volts (eV).
[c] Debye.

The electropositive amine proton of N-protonated R-deprenyl (R-dep) (Fig. 2B) contributed to the formation of the lowest unoccupied molecular orbital (Fig. 2C). The charges of amine proton of R-dep and carbon atom of C_{70} are modified in complex **4**. The distance between the carbon atom of C_{70} and the amine proton of R-dep in complex **4** was 2.5 Å. Accordingly the interaction is between amine proton and the sp^2 carbon atom (N–H···C=C) (Fig. 2D) and is of electrostatic type.

Fig. 3 shows the electronic density surfaces and the significant charges of C_{70} derivative (**2**) alone and of its complex with R-dep (**5**). The R-dep amine proton and carboxylate oxygen of C_{70} derivative modified their charges in complex **5**. The charges of the amine proton of R-dep and carboxylate oxygen of C_{70} derivative were 1.7 Å (Fig. 3B). Accordingly, the interaction is between amine proton of R-dep and lone pair of carboxylate oxygen of fullerene derivative (N–H···O=C) and is a moderate hydrogen bond type of interaction.

The common feature of interaction of R-dep (**3**) with C_{70} (**1**) and its derivative (**2**) was the decrease of total energy in their respective complexes **4** and **5**, as shown in Table 2. This is in good agreement with the Hartree–Fock energies for atoms, where it has been observed that energy diminishes when the number of atoms increases [20].

The binding energy of [5,6]fullerene-C_{70} (**1**) with R-dep (**3**) is 14.3 kcal/mol, calculated as the energy difference between the total energy of **4** and the sum of the total energies of **1** and **3**. Similarly, the binding energy of C_{70} derivative (**2**) with R-dep (**3**) is 17.8 kcal/mol, calculated as the energy difference between the total energy of **5** and the sum of the total energies of **2** and **3**. Accordingly, it is concluded that the complex **5** formed between diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate and R-dep is more stable than complex **4** formed between [5,6]fullerene-C_{70} and R-dep.

The LUMOs of all the compounds along **1**–**5** have higher in energy than their respective HOMOs. This is in good agreement with the Fukui Postulate [21], as the electrons in the orbital with the higher energy are more susceptible to receive the nucleophilic species, whereas the electrons in the orbital with the lower energy are more susceptible to receive the electrophilic species.

The hardness values clearly indicate that molecule **3** (R-dep) is harder than rest of the molecules. This is because of the electropositive nature of it. The hardness values in complexes **4** and **5** are lower than the value of hardness recorded for R-dep.

The dipole moments (μ) of the complexes **4** and **5** are larger than their respective chiral selectors **1** and **2** since the addition of polar R-dep analyte modifies the charge distribution in the complexes.

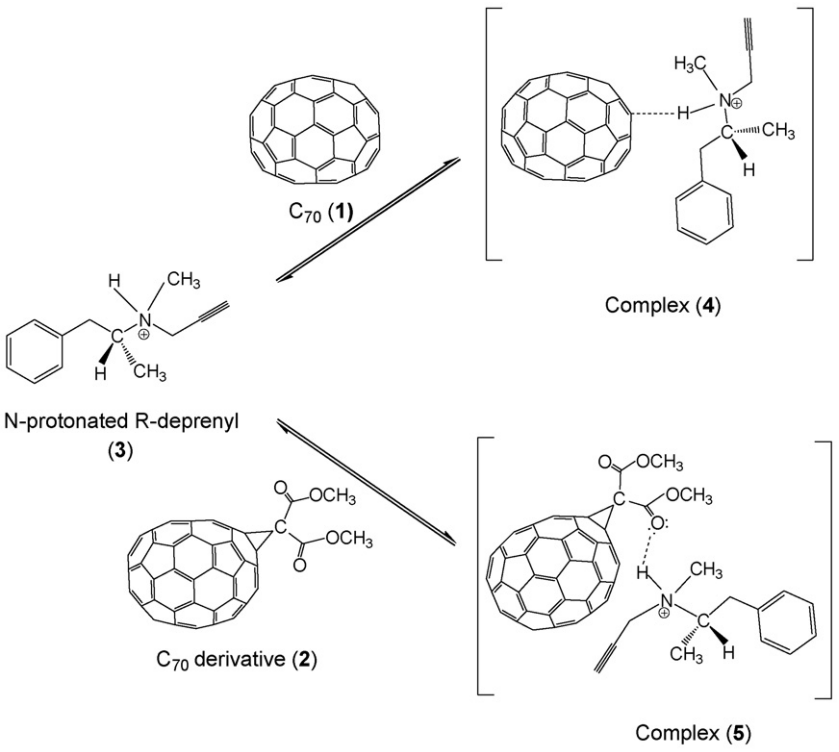

Fig. 4. The complex **4** is formed between N-protonated R-deprenyl and C_{70} fullerene; the interaction is between amine proton and the sp^2 carbon atom (N–H···C=C). The complex **5** is formed between N-protonated R-deprenyl and C_{70} derivative; the interaction is between amine proton and lone pair of carboxylate oxygen atom (N–H···O=C).

This implies the interaction between chiral selector and the analyte R-deprenyl.

The structural stability and feasibility of all the compounds (**1**–**5**) was assessed by computing their harmonic normal modes of vibration. The lowest-lying normal mode of vibration of each of the compounds **1**–**5** is of frequency at 224.25, 25.97, 32.94, 9.53 and 14.46 cm^{-1}, respectively. The absence of imaginary frequencies indicates that the structures of all the compounds are the local minima.

The total energy, frontier orbital energies, dipole moment, atomic charges, hardness and intermolecular forces were helpful to provide a logical description of the nature in which the mechanism of complexation between R-deprenyl and C_{70} or C_{70} derivative occurs.

The mechanism of the potential development is based on the formation of a complex between R-deprenyl and chiral selector [5,6]fullerene-C_{70} or diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate. Accordingly with the theoretical calculation, diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate is forming a more stable complex with R-dep than [5,6]fullerene-C_{70}. This is in agreement with the experimental results, because the highest value of the slope was obtained for the enantioselective, potentiometric electrode based on the diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate, proving the new theory of potential development: the highest the stability of the complex formed between R-deprenyl and chiral selector, the highest the slope of the electrode [22]. The actual interactions between R-deprenyl and C_{70} fullerenes are shown in Fig. 4.

3.2. The effect of pH on the response of the electrodes

The influence of the pH values on the response of the proposed electrodes was investigated by recording the emf of the cell for solutions containing 10^{-6} mol/L R-deprenyl at pH values between 1 and 12. The plot of E (mV) versus pH (Fig. 5) indicates that the response of the electrode does not depend on the pH changes in the pH ranges 3.0–11.0 for both enantioselective, potentiometric electrodes.

3.3. The selectivity of the proposed electrodes

The selectivity of the potentiometric electrodes was investigated using mixed solution method. S-Deprenyl, polyvinylpyrolidone (PVP), creatine, creatinine, paracetamol and L-glutamic acid were selected as possible interferences. The ratios between the concentrations of interfering ions and R-deprenyl were 10:1. The values of the potentiometric selectivity coefficients (Table 3) indicate that the electrodes can be reliably used for enantioanalysis of R-deprenyl in biological samples as well as in its pharmaceutical formulation due to the good selectivity and enantioselectivity that they exhibited. The selectivity of the proposed EPMEs is higher than the one obtained using the EPMEs based on maltodextrines [19].

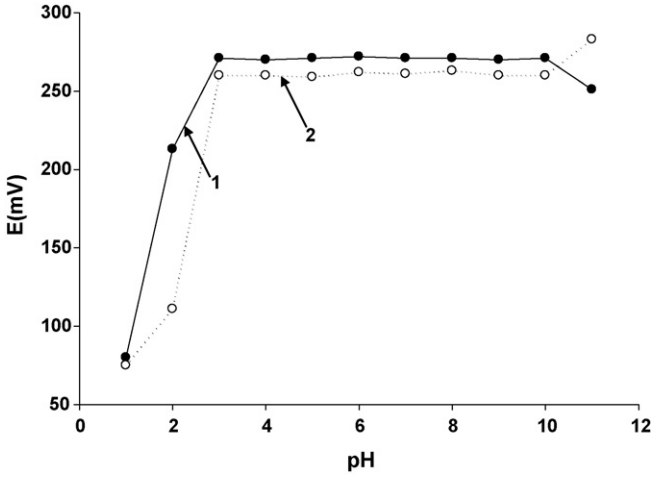

Fig. 5. The influence of pH on the response of the enantioselective potentiometric electrodes based on (**1**) [5,6]fullerene-C_{70} and (**2**) diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate for the assay of R-deprenyl ($C_{R\text{-}dep} = 10^{-6}$ mol/L).

3.4. Analytical applications

The assay of R-deprenyl in the presence of S-deprenyl was carried out using different ratios between R- and S-deprenyl. The results obtained (Table 4) confirmed once more the suitability of the proposed potentiometric electrode for the enantioanalysis of R-deprenyl. No significant difference in the recovery values were recorded for the different ratios between the enantiomers, because the calculated t values were all lower than the tabulated $t = 2.262$.

The results obtained for content uniformity test of Lentogesic tablets using the proposed electrode showed, that the tested pharmaceutical formulation contain 1.50% (RSD = 0.16%, $n = 10$) and 1.59% (RSD = 0.16%, $n = 10$) R-deprenyl, when the electrodes based on [5,6]fullerene-C_{70} and on diethyl (1,2-methanofullerene C_{70})-

Table 3
Potentiometric selectivity coefficients for the proposed electrodes[a].

Electrode based on	K^{pot}_{Sel}					
	Interfering species (J)					
	S-dep	PVP	Creatine	Creatinine	Paracetamol	L-Glutamic acid
1	4.1×10^{-4}	6.8×10^{-3}	2.6×10^{-3}	1.7×10^{-3}	1.7×10^{-3}	4.0×10^{-4}
2	8.1×10^{-4}	4.0×10^{-4}	1.7×10^{-3}	3.1×10^{-3}	$\ll \times 10^{-4}$	$\ll \times 10^{-4}$

[a] All measurements were made at room temperature; all values are the average of 10 determinations.

Table 4
Determination of R-deprenyl in the presence of S-deprenyl[a].

Electrode based on	Recovery, R-deprenyl (%)				
	R:S				
	2:1	1:1	1:2	1:4	1:9
1	99.95 ± 0.02	99.62 ± 0.01	99.87 ± 0.02	99.94 ± 0.02	99.97 ± 0.01
2	99.15 ± 0.01	99.16 ± 0.02	99.16 ± 0.02	100.00 ± 0.01	99.92 ± 0.02
t-Test[b]	2.098	2.023	2.055	2.025	2.030

[a] All measurements were made at room temperature; all values are average from 10 measurements.
[b] Values determined at 95% confidence level (tabulated $t = 2.262$).

71-71-dicarboxylate, respectively, were used. The average recovery values were in agreement with that obtained using a capillary electrophoresis method: $1.47 \pm 0.21\%$.

4. Conclusions

To confirm the electroanalytical experimental results, computational calculations were carried out using ab initio theory. Based on the results obtained from theoretical calculations it is concluded that the enantiomeric selectivity is endowed by the two intermolecular forces of interactions to confer stability: electrostatic interaction and moderate hydrogen bond interaction. Thus, we proved experimentally as well as theoretically that the complex formed between diethyl (1,2-methanofullerene C_{70})-71-71-dicarboxylate and R-dep is the most stable one.

The proposed electrodes exhibited slopes very closed with the Nernstian value, high enantioselectivity and selectivity, low limits of detection and wide working concentration ranges. The high reliability of the analytical information obtained using these electrodes are due to the high reliability of carbon paste based electrodes' design.

References

[1] H.Y. Aboul-Enein, I.W. Wainer, The Impact of Stereochemistry on Drug Development and Use, Wiley, New York, 1997.
[2] J. Knoll, Z. Ecseri, K. Kelemen, J. Nievel, B. Knoll, Arch. Int. Pharmacodyn. Ther. 155 (1965) 154–164.
[3] K. Magyar, E.S. Vizi, Z. Ecseri, J. Knoll, Acta Physiol. Hung. 32 (1967) 377–387.
[4] J. Knoll, K. Magyar, in: E. Costa, M. Sandler (Eds.), Monoamine Oxidases—New Vistas Adv. in Biochem. Psychopharmacol., Raven Press, New York, NY, 1972, pp. 393–408.
[5] L.G. Hársing Jr., K. Magyar, K. Tekes, E.S. Vizi, J. Knoll, Pol. J. Pharmacol. Pharm. 31 (1979) 297–307.
[6] K. Tekes, L. Tóthfalusi, J. Gaál, K. Magyar, Pol. J. Pharmacol. Pharm. 40 (1988) 653–658.
[7] K.J. Magyar, Neural Transm. Suppl. 41 (1994) 167–175.
[8] E. Szoko, T. Tabi, A.S. Halasz, M. Palfi, H. Kalasz, K. Magyar, Chromatographia 60 (2004) S245–S252.
[9] T. Tabi, A.S. Halasz, M. Palfi, K. Magyar, E. Szoko, J. Chromatogr. Sci. 42 (2004) 21–26.
[10] T. Tabi, K. Magyar, E. Szoko, Electrophoresis 24 (2003) 2665–2673.
[11] E.M. Kim, H.S. Chung, K.J. Lee, H.J. Kim, J. Anal. Toxicol. 24 (2000) 238–244.
[12] E. Szoko, K. Magyar, J. Chromatogr. A 709 (1995) 157–162.
[13] H. Kalász, T. Bartók, R. Komoróczy, É. Szöko, D. Haberle, J.P. Kiss, E. Hennings, K. Magyar, S. Fürst, Curr. Med. Chem. 6 (1999) 215–222.
[14] D. Haberle, H. Kalasz, I. Hollosi, J. Puscok, T. Csermely, K. Magyar, E. Toth-Molnar, Chromatographia 50 (1999) 415–422.
[15] Z. Tarjanyi, H. Kalasz, G. Szebeni, I. Hollosi, M. Bathori, S. Furst, J. Pharm. Biomed. Anal. 17 (1998) 725–731.
[16] T. Csermely, H. Kalasz, K. Rischak, M. Bathori, Z. Tarjanyi, Z. Gyarmati, S. Furst, J. Planar Chromatogr. Mod. TLC 11 (1987) 247–253.
[17] Spartan'04 Version 1.0.3, Wavefunction, Inc., Irvine, CA, USA, 2004.
[18] T. Sokalski, A. Ceresa, M. Fibbioli, T. Zwickl, E. Bakker, E. Pretsch, Anal. Chem. 71 (1999) 1210–1214.
[19] R.I. Stefan-van Staden, T.R. Mashile, Instrum. Sci. Technol. 35 (2007) 117–123.
[20] S.R. Gadre, S.B. Sears, S.J. Chakravorty, R.D. Bendale, Phys. Rev. A 32 (1985) 2602–2606.
[21] K. Fukui, Science 218 (1982) 747–754.
[22] R.I. Stefan, H.Y. Aboul-Enein, Instrum. Sci. Technol. 27 (1999) 105–110.