Zagazig J. Pharm. Sci., December 2007 ISSN 1110-5089
Vol. 16, No. 2, pp. 1-7

RELATIVE SELECTIVITY COEFFICIENT AS A NEW CONCEPT FOR EVALUATING ELECTROCHEMICAL DOPAMINE SENSORS

Mohsen M. Zareh
Department of Chemistry, Faculty of Science, Zagazig University, Zagazig 44519, Egypt

ABSTRACT

Two types of electrochemical sensor were introduced for the selective determination of dopamine. Both potassium tetraflorophenyl borate (K-TFPB) and a synthesized N,N-bis-ethoxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane (DZCE) were used as charged ionophore and a neutral carrier. The calibration graphs of the obtained electrodes showed satisfactory Nernstian slopes (57.8, 58.4 mV/decade). They work linearly 9×10^{-3}-7.9×10^{-6} M DAH^+ within a pH value 3.5-8.3 for both electrodes. Selectivity coefficients of the studied electrodes were calculated towards several inorganic cations, aminoacids, and pharmaceutical compounds. The Relative Selectivity Coefficient (RSC) was introduced and was applied for evaluating the selectivity properties of dopamine electrode using mathematical equation. Average Relative Selectivity Coefficient (ARSC) and Total Average Relative Selectivity Coefficient (TARSC) were defined and calculated as new parameters for each electrode. An improvement of the selectivity coefficient values was observed when DZCE was added as neutral carrier to the membrane constituents. The electrode was applied for the determination of dopamine in its pharmaceutical preparations and in banana pulp. The obtained results were compared with those obtained by a previously reported spectrophotometric method.

INTRODUCTION

Dopamine (DA) has the chemical formula ($C_8H_{11}NO_2$). Its chemical name is 4-(2-aminoethyl)benzene-1,2-diol and it is abbreviated as "DA"[1]. It belongs to the catecholamine family; it is a precursor to epinephrine (adrenaline) and then norepinephrine (noradrenaline) in the biosynthetic pathways for these neurotransmitters. Dopamine can be supplied as a medication that acts on the sympathetic nervous system, producing effects such as increased heart rate and blood pressure.

Different methods were used for the determination of dopamine. FIA and HPLC with chemiluminence detection was applied for determination of DA by Nalewajka *et al.*[2]. Catecholamines were determined by the spectrophotometric method based on the use of Poly(dimethylsiloxane) (PDMS) technology[3]. Abdulrahman *et al.*[4] reported a flow injection-spectrophotometeric determination of some catecholamine drugs via oxidative coupling reaction with *p*-toluidine and sodium periodate.

Glassy carbon electrodes were applied for the determination of dopamine. A sensitive and selective electrochemical method for the determination of DA was developed using a calix-4-arene crown-4 ether film modified glassy carbon electrode[5]. The Si-TiPH bulk modified carbon paste electrode[6] and Nafion coated carbon paste electrode[7] was used for the selective determination of DA in the presence of ascorbic acid. Electrocatalytic oxidation and selective detection of dopamine at a 5,5-ditetradecyl-2-(2-trimethyl-ammonioethyl)-1,3-dioxane bromide self-assembled bilayer membrane modified glassy carbon electrode was introduced by Lin and Gong[8]. Hayashi et al.[9] succeeded in detecting DA in the presence of L-ascorbic acid using interdigitated electrode array. Cheng et al.[10] applied fiberion carbon-fiber electrode for in vivo determination of concentration of cationic neurotransmitter dopamine.

Several authors constructed amperometric sensors for dopamine. Cu–dipyridyl complex was applied for preparing amperometric DA-sensors [11]. Tu and Chen[12] applied nano-disposable biosensors. Plant tissue containing oxidizing enzyme was used to build up biosensor for determination of dopamine and other catechol amines[13].

Some previous researches were reported for determination of DA using ion-selective electrodes. Calix-3-arene derivative was applied for preparing DA-selective electrode[14]. Junior et al.[15] constructed FIA-potentiometric sensor for dopamine based on poly (ethylene-co-vinyl acetate)-Cu (II) ion. Othman et al.[16] prepared PVC-membrane electrodes based on 12-crown-4-phosphotungestic and 12-crown-4-TPB ionophores for dopamine determination. Montenegro and Sales analysed dopamine either by an indirect method using periodate selective electrode[17] or by direct method using dopamine selective electrode[18] based on tetra-chlorophenylborate. Earlier, Liu and Yu[19] applied crown ethers as neutral ionophores for preparing electrodes for primary amine.

In fruits, dopamine is the substrate for Polyphenol Oxidases (PPOs). These are a family of enzymes responsible for browning of fresh fruits and vegetables when they are cut or bruised. This help to protect damaged fruit and vegetables against growth of bacteria and fungi[20].

In the present study, synthesized Diaza Crown Ether derivative (DZCE) was used for the first time as a sensor for preparing an ion-selective electrode for dopamine. A comparison between the properties of the diaza crown and the usual crown ether based electrodes was established. The new electrode allows the direct determination of dopamine without pre-separation using toxic solvents or expensive instrumentation like in HPLC. No need of liquid nitrogen like in polarographic methods. Ascorbic acid and uric acids were not interfering in dopamine determination by this electrode which is recorded when using carbon paste electrodes. An improvement of selectivity was found after adding synthesized Diaza Crown Ether (DZCE) derivative to the potassium *tetra-kis*-[3,5-*bis*-(trifloromethyl)phenyl] borate (TFPB). Another new point is that the evaluation of selectivity properties was applied by introducing the idea of Relative Selectivity Coefficient "RSC".

For correspondence: *email:* mohsenzareh@hotmail.com

EXPERIMENTAL

Synthesis of the host molecule:

DZCE was synthesized according to the procedure described previously[21]. It depends on the addition of (5.84 g) of *N,N'-bis*-ethoxycarboxycarbonyl-1,8-diamino-3,6-dioxaoctane in dry dimethyl sulfoxide DMS (75 ml) dropwisely to a stirred suspension of sodium hydride (1.12 gm) in dry dimethyl sulfoxide (125 ml). After 3 hours, 10 gm of triethylene glycol bis-p-sulfonate in dry DMS was added to the formed solution and the mixture was sit aside for 3 days under N_2. Then, 2N HCl was added and the mixture was extracted in $CHCl_3$. The organic extract was washed with water, dried in $MgSO_4$ and evaporated. The residual oil was purified by chromatography on silica. The macrocycle DZCE was obtained as solid (m.p. 75-78°C). The structure of the obtained compound was verified by elemental analysis and IR (found C, 52.9; H, 7.1; N, 8.4%; confirm $C_{18}H_{34}N_2O_8$; ν_{max} 1680 cm^{-1}).

Reagents and materials:

The used materials for preparing the electrodes were Tetrahydrofuran (THF) (Merck) (after its distillation), Dodecyl Phthalate (DDP) (Fluka), potassium *tetra-kis*-[3,5-*bis*-(trifloromethyl)-phenyl]-borate (KTFPB) (Fluka), high molecular weight Poly(vinylchloride) (PVC) (Fluka), and *N,N'-bis*ethoxycarbonyl-1,10-diaza-4,7,13,16-tetra-oxacyclo-octadecane (diaza-18-crown-6) (DZCE) (synthesized as aforementioned) were used for the preparation of all membranes. Dopamine (4-(2-aminoethyl)benzene-1,2-diol) (Sigma), ephedrineHCl (Sigma), adrenaline (Sigma), caffeine (Sigma), pilocarpine hydrochloride (Sigma), atropine sulfate (Sigma); adrenaline (Sigma), ascorbic acid, urea, glycine, arginine, and sodium glutamate (Aldrich) were used. Dopamine injection ampoules (40 mg/5ml) were purchased from the local drug stores. Nitrate salts of inorganic cations (Na^+, K^+, Li^+, NH_4^+, Ca^{++}, Mg^{++}, and Ba^{++}) were purchased from (Fluka). De-ionized water was operated through the whole work for the preparation of different solutions and for rinsing the electrodes.

Instruments:

The cell e.m.f. values were measured using a bench top model Sension-4 (HACH, Loveland, Colorado, USA). The instrument was loaded to a computer system through RS-232 connection and HACH-software. The same instrument was applied for pH-measurements.

The spectrophotometric measurements were carried by a UV-VIS-spectrophotometer DR-4000 (HACH, Loveland, Colorado, USA), loaded to a computer system through RS-232 connection and HACH-software.

Electrode system and potentiometric measurements:

1mg KTFPB or (1mg KTFPB + 2mg DZCE) were applied as sensor materials for membranes I and II, respectively. The mentioned ionophores were mixed with 60-67 mg DDP plasticizer and 30-31.5 mg PVC. The membrane was prepared according to a procedure described before[21]. The membrane discs were mounted on electrode Phillips bodies (type IS 561, Eindhoven, Netherlands) for electromotive force measurements. The electrode was filled with an aqueous inner filling solution (0.01 M KCl and 0.01 M DAHCl solution).

The potentiometric measurements were performed at room temperature (25°C) in a Galvanic cell, which can be represented as the following:

Ag-AgCl/Li-acetate/sample//ion-selective membrane// inner filling solution/ Ag-AgCl

The outer compartment of the reference electrode was filled with 0.1M lithium acetate solution.

The potential was measured by immersing the electrodes with a reference Calomel into 50 ml water. Different aliquots of 10^{-2} and 10^{-1} M DAHCl were added to cover a concentration range of (10^{-7}-10^{-2} M DAH^+). The potential values were recorded and plotted versus p[DAH^+] using (Microsoft Excel 2003). For studying the pH-effect on the electrode potential, the pH was changed using 0.1M NaOH or HCl. The potential values were recorded at different pH for the electrodes in 10^{-4}, 10^{-3}, and 10^{-2} M DAH^+ solutions.

The selectivity coefficient values for several cations (Na^+, K^+, Li^+, NH_4^+, Ca^{++}, Mg^{++}, and Ba^{++}), aminoacids (glycine, arginine, and sodium glutamate) and pharmaceutical amines (ephedrine hydrochloride, adrenaline, caffeine, pilocarpine hydrochloride, and atropine sulfate) were calculated (table 1) by the use of the Separate Solution Method (SSM)[23]. The e.m.f. of 0.01 M of the interference solution and that for the same concentration of DAH^+ solution were measured. Then, the selectivity coefficient values of electrodes ($K_{i,j}^{pot}$) were estimated for the different interferents according to the equation: $\log K^{pot}_{DAH^+,J^{z+}} =$

$$(E_j - E_{DAH^+})/S + [1-(Z_{DAH^+}/Z_j)] \log a_{DAH^+} \quad \text{.....(1)}$$

Where E represents the emf readings for the primary ion DAH^+ and the interfering ion (J^{z+}); and S is the observed Slope for the primary ion.

Table (1): Selectivity coefficient values ($K_{DAH^+,J^{z+}}$) for both dopamine electrodes based on TFPB (type-I) and diazacrown ether analogues (type-II).

Interferent	$K_{DAH^+,J^{z+}}$	
	I	II
Na^+	7.05×10^{-6}	4.25×10^{-6}
K^+	4.66×10^{-5}	3.14×10^{-5}
Li^+	1.30×10^{-6}	7.9×10^{-7}
NH_4^+	1.12×10^{-5}	7.19×10^{-6}
Ca^{++}	1.01×10^{-5}	8.59×10^{-6}
Mg^{++}	4.62×10^{-6}	3.78×10^{-6}
Ba^{++}	2.22×10^{-5}	1.92×10^{-5}
Glycine	2.0×10^{-6}	1.31×10^{-6}
Arginine	2.3×10^{-6}	1.83×10^{-6}
Sodium glutamate	1.31×10^{-5}	9.0×10^{-6}
Ascorbic acid	1.92×10^{-3}	7.34×10^{-4}
Uric acid	2.36×10^{-3}	1.53×10^{-3}
Caffeine	1.10×10^{-7}	6.0×10^{-8}
Pilocarpine	6.38×10^{-3}	4.71×10^{-3}
Ephedrine	2.20×10^{-2}	1.63×10^{-2}
Atropine	6.43×10^{-2}	4.63×10^{-2}
Adrenaline	3.15×10^{-2}	2.31×10^{-2}

ISSN 1110-5089

5 ml injection ampoules of dopamine HCl (products of EIPICO, Egypt; Ebewe Pharma, Austria; or Pierre Fabre, France) were diluted to 50 ml solutions. The obtained solutions were transferred to the potentiometic cell. Both DAH^+-selective and the reference electrodes were immersed into the solutions and the cell e.m.f. was measured. The potential readings of the sample solutions were compared to previously prepared calibration graph under the same condition.

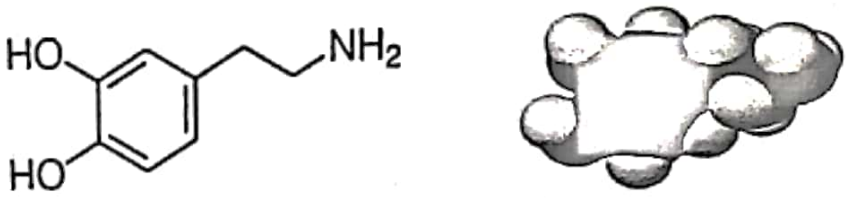
20g (fresh weight) of sliced banana (two days ripened) were transferred to a beaker containing 20 ml 0.1M HCl. The mixture was homogenized in a blender. The homogenate was centrifuged for 20 minutes. The supernatant solution was adjusted to pH 4 using K_2CO_3, then brought up to 50 ml. The solution was transferred to the potentiometric cell and subjected for e.m.f.-measurements using the proposed electrode. The obtained values were compared to a calibration graph of dopamine standard solutions treated typically like the measured samples.

For the spectrophotometric analysis, after extraction as aforementioned, purification step was applied. It was performed by elution of 5 ml of the extract into a Dowex 50 X-8 column, which was washed with 20 ml 2N HCl, 5 ml water, 10 ml 1N acetate-acetic buffer (pH 6), and finally with 5 ml water. The dopamine was eluted by 6 ml 1N HCl at rate of 0.25 ml /minute, followed by 6 ml 2N HCl. The eluted dopamine was assayed according to procedures mentioned by Abdulrahman et al[4]. It is based on the oxidative coupling with p-toluidine (0.008% w/v) and sodium periodate (0.4mM) giving an orange dye with maximum absorption at 480 nm. The obtained results were compared to a calibration graph previously prepared for dopamine solutions (2-50 µg/ml) under the same conditions.

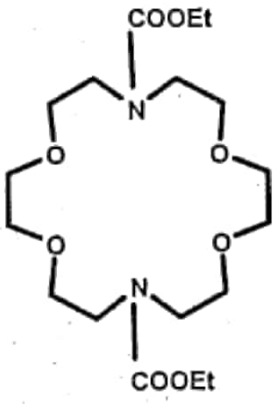
RESULTS AND DISCUSSION

Effect of membrane composition:

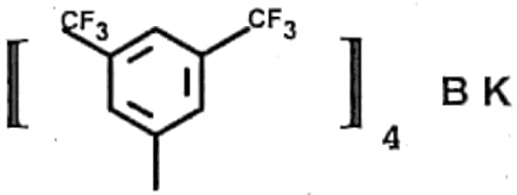
Different compositions were tried to optimize the best membrane composition. Of them, two electrodes with different membrane compositions were prepared. One has a membrane containing KTFPB (type-I), and the other constitutes (KTFPB+DZCE) (type-II). Both electrodes exhibit typical Nernstain slope (57.8 and 58.4 mV/decade). They work linearly in a concentration range 9.0×10^{-3} - 7.9×10^{-6} M DAH^+. The calibration graphs representing both electrodes are displayed in figure 2. The lower linear limit of the calibration graph for electrode II is better than that of electrode I. This is because the ion-pair in electrode-II contains a cavity, which helps the chelation of DAH^+. The DZCE works like the charge carrier that helps the ion-association with TFPB.



Dopamine (DA)



N, N-bisethoxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane (DZCE)



Potassium tetrakis[3,5-bis(trifloromethyl)-phenyl] borate (KTFPB)

Figure (1): Structural formulas of Dopamine (DA), *N,N-bis*ethoxycarbonyl-1,10-diaza-4,7,13,16-tetraoxacyclo-octadecane(DZCE), and potassium *Tetrakis*[3,5-*bis*-(trifloro-methyl)-Phenyl] Borate (TFPB)

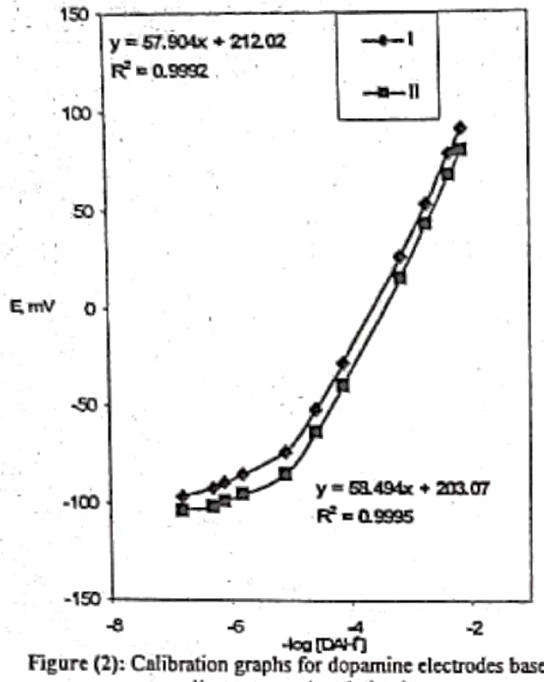


Figure (2): Calibration graphs for dopamine electrodes based on diazacrown ether derivative

The mechanistic equation that represents the exchange reaction at the membrane-solution interface for electrode-I is written as below:

$[DAH]^+ + [TFPB]^- \rightleftharpoons [TFPB^- DAH^+]$

$K_{ex} = [TFPB^- DAH^+] / [DAH^+][TFPB^-]$

In case of electrode-II, the following equilibrium is expected:

$[TFPB]^- K^+ + DZCE \rightleftharpoons [(DZCE\text{-}K)^+ TFPB^-]$

$[(DZCE\text{-}K)^+ TFPB^-] + DAH^+ Cl^- \rightleftharpoons [(DZCE\text{-}DAH)^+ TFPB^-] + KCl$

$K_{ex} = [(DZCE\text{-}DAH)^+ TFPB^-]/([(DZCE\text{-}K)^+ TFPB^-][DAH^+])$

The dynamic response of both electrodes showed instantaneous and stable potential readings. Figure 3 displays the obtained results.

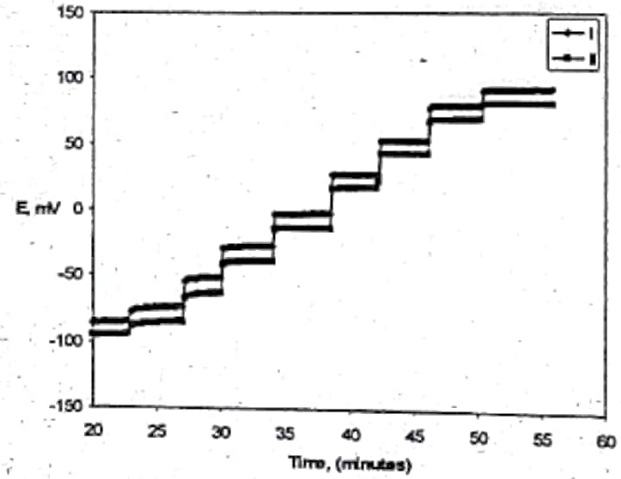


Figure (3): Dynamic response of dopamine electrodes based on diazacrown ether derivative

Effect of pH:

To optimize the condition of measurements, the effect of pH on the potential was studied. The corresponding curves for both electrodes (I and II) are shown in figure 4. The working pH-range is 3.5-8.3 for both electrodes for 10^{-2} M DAH^+. Whenever 10^{-3} M DAH^+ solution was measured, the plateau potential values were between 2.9 and 9.1. This is a wide pH-range compared to the previous electrodes, which are not working in alkaline medium (2.5-6 and 3.5-6). The formation of the free base is the reason of the break in the basic part of the plateau. This depends on the concentration of DAH^+. In acidic medium, the hydrogen ion interference is the reason of the curve break.

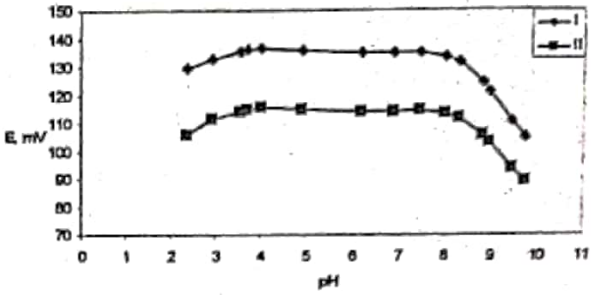


Figure (4): Effect of pH on the potential of dopamine electrodes based on either TFPB and TFPB + DZCE in 0.01M dopamine solution

Validation of the method:

Linearity:

The linearity was studied in the concentration range of 10^{-7} up to 10^{-2} M DAHCl. The calibration graph is representing the plot of the cell e.m.f. against -log M (pM) of DAHCl solutions. Each point of the curve is the mean value of four measurements. The regression equation of calibration graph of the two electrodes (I and II) can be written as below:

$y = 57.0904x + 212.02$, and $y = 58.494x + 203.07$

The corresponding correlation coefficients are 0.9992 and 0.9995 for each case.

Limit of detection and quantification:

The limit of detection of both electrodes is calculated according to the ISE definition[23]. The obtained values were 6.31×10^{-6} and 7.94×10^{-6} M for electrodes I and II, respectively.

The Limit Of Quantification (LOQ) was calculated according to ICH Q2B recommendation[24]. The obtained values are 7.9×10^{-6} M for both electrodes.

t-test and F-test:

The student's t-test and F-test were performed for the determination of dopamine in its injection solutions and in the ripened banana by using electrode-II. t-values were 0.48 and 0.94, and the f-values are 0.98 and 0.89, respectively.

Selectivity and Relative Selectivity Coefficient (RSC):

The selectivity coefficient values ($K_{DAH^+,j}^{pot}$) for the common inorganic cations, amino acids, pharmaceutical amines were calculated and recorded in table 1. It is shown that the values of the selectivity coefficients for the inorganic cations range between 10^{-5} and 10^{-7}. This shows a super selectivity properties. Amino acids like glycine, arginine, glutamate showed values of the selectivity coefficient of the order of 10^{-5}-10^{-6}. This is because the presence of the Zwitter ion masked the amine group from being part of chelation with the DZCE. This favors the discrimination of DPH^+ over them. In case of ascorbic acid, uric acid and other pharmaceutical amines (pilocarpine, adrenaline, ephedrine, and atropine), the selectivity coefficient values were of the order of 10^{-2}-10^{-3}. Although these values are higher than those for other cations, they still suitable for measuring dopamine in their presence.

The relative selectivity coefficient "K_{rel}" is a parameter introduced to evaluate selectivity properties of

ISSN 1110-5089

electrodes or sensors of different composition, but responding to the same ion. This factor helps the mathematical comparison of selectivity properties between these sensors or electrodes. Relative selectivity coefficient can be calculated by the following steps:

The selectivity coefficient values of an electrode I ($K_{i,j}^{pot}$) is calculated either by the SSM or the FSM[22] for the different interferents. Under the same conditions, the selectivity coefficient values of electrode II ($K_{i,j}^{pot}$) is calculated for the same interferents.

If there are only two electrodes I and II, the value of the Relative Selectivity Coefficient (RSC) of electrode (I) toward electrode (II) can be represented in the following equation for one interferent:

$$(K_{rel})_{I:II} = (K_{i,j}^{pot})_I / (K_{i,j}^{pot})_{II} \quad \text{.....(2)}$$

Where $(K_{i,j}^{pot})_I$ and $(K_{i,j}^{pot})_{II}$ are the usual selectivity coefficients for electrodes (I) and (II) toward one interferent cation. $(K_{rel})_{I:II}$ is the relative selectivity coefficient values for electrode I toward electrode II.

By the same way, the RSC for electrode II can be calculated toward electrode I:

$$(K_{rel})_{II:I} = (K_{i,j}^{pot})_{II} / (K_{i,j}^{pot})_I \quad \text{.....(3)}$$

If there are (n) interferents, $(K_{rel})_{II:I}$ must be calculated n times.

The Average Relative Selectivity Coefficient (ARSC) for electrode I toward electrode II, $(K_{I:II})_{av}$ can be calculated as below for (n) number of interferent ions:

$$(K_{rel\text{-}I:II})_{av} = [\sum_{1 \to n} (K_{rel})_{I:II\text{-}n}]/n \quad \text{.....(4)}$$

For calculating the Average Relative Selectivity Coefficient (ARSC), $(K_{rel\text{-}II:I})_{av}$, for electrode II toward electrode I, similar equation can be applied.

$$(K_{rel\text{-}II:I})_{av} = [\sum_{1 \to n} (K_{rel})_{II:I\text{-}n}]/n \quad \text{.....(5)}$$

The value of the RSC (equations 2 and 3) indicates which electrode has the better selectivity properties toward the tested interferent. If $(K_{rel})_{I:II} < 1$, this means that electrode (I) has better selectivity than electrode (II). If $(K_{rel})_{I:II} > 1$ the electrode (I) has worse selectivity than electrode (II). If $(K_{rel})_{I:II} = 1$, both electrodes have equal selectivity.

Finally, general formula can be derived to compare between one electrode (X) and many electrodes (1, 2,3,...,m):

$$(K_{rel\text{-}X})_{total} = [(K_{rel\text{-}X:1})_{av} + (K_{rel\text{-}X:2})_{av} + (K_{rel\text{-}X:3})_{av} + (K_{rel\text{-}X:4})_{av} + \ldots + (K_{rel\text{-}X:m})_{av}]/(m) \quad \text{.....(6)}$$

Where X is the electrode under study; (1, 2, 3, 4,....m) refers to the number of electrodes to be compared with; $(K_{rel\text{-}X})_{total}$ is the average of the relative selectivity coefficient (TARSC) for X-electrode toward all electrodes; $(K_{rel\text{-}X:1})_{av}$ is the Average of Relative Selectivity Coefficient (ARSC) of X-electrode towards electrode-1 for all interferents. It can be predicted that the smaller the $(K_{rel\text{-}X})_{total}$-value, the better the selectivity properties of an electrode.

The selectivity coefficient values are shown in table 1. The values (K_{DAH^+, I^-}^{z+}) for electrode II is lower than those for electrode I. This means a better selectivity for electrode II than electrode I is expected. Nevertheless, this is not enough to discriminate between the selectivity of the two electrodes. Therefore, evaluation of selectivity properties was conducted by applying the aforementioned "relative selectivity rules".

Generally, it can be reported that the selectivity coefficient values of electrode II has numerical values less than that for electrode I by a factor 1/2. This factor is the value of the relative selectivity coefficient RSC for electrode II toward electrode I $(K_{rel})_{II:I}$. For the inorganic cations, the average $(K_{rel})_{II:I}$ is 0.722, while for organic amines it is 0.702. This shows that the selectivity properties of electrode II is better than that of electrode I toward these cations. This is caused by the association of the formed ion-pair by the host DZCE-molecule, which led to more stability of the formed DAH^+-complex.

Likewise, by using the RSC-concept the selectivity properties of electrode I can be compared to the previously reported[16] electrodes (pre1), and (pre2). Where pre1 and pre2 refer to the previously reported electrodes with Crown Ether-Phosphotungestic Acid (CE-PTA) and Crown Ether-Tetraphenyl-Borate (CE-TPB) ion pairs, respectively. The Total Average Relative Selectivity Coefficients (TARSC) values for electrode I are $(K_{rel})_{I:pre1}$: 9.9×10^{-3}, and $(K_{rel})_{I:pre2}$: 5×10^{-3}. By the same way, electrode II is compared to previously reported electrodes (pre1) or (pre2). It is found that $(K_{rel})_{II:pre1}$ is 6.7×10^{-3} and $(K_{rel})_{II:pre2}$ is 3.4×10^{-3} i.e. the present electrode exhibits better selectivity properties than the previously reported electrodes.

The application of the proposed electrode for the determination of dopamine in its pharmaceutical preparations was established. Samples of injection solutions from different companies were subjected to the electrode analytical procedures. Table 4 shows the obtained results. The recovery showed values between 98.6 and 100.1%. The obtained results agreed with those obtained by applying the previously reported spectrophotometric method[4].

Table (2): Relative Selectivity Coefficient (RSC) values for both I and II dopamine electrodes towards each other.

Interferent	RSC (K_{rel})	
	$(K_{rel})_{I:II}$	$(K_{rel})_{II:I}$
Na^+	1.65	0.603
K^+	1.48	0.674
Li^+	1.65	0.604
NH_4^+	1.56	0.639
Ca^{++}	1.17	0.854
Mg^{++}	1.22	0.818
Ba^{++}	1.15	0.864
Glycine	1.53	0.651
Arginin	1.25	0.794
Sodium glutamate	1.46	0.682
Caffeine	1.68	0.593
Pilocarpine	1.35	0.738
Ephedrine	1.35	0.740
Atropine	1.38	0.721
ARSC	1.43	0.712

Table (3): Relative Selectivity Coefficient (RSC) values for the present electrodes I and II toward the previously reported [16] electrodes (pre1) or (pre2) based on either CE-PTA or CE-TPB respectively.

Interferent	$K_{DAEH^+,J^{z+}}$, Previous electrodes [16]		RSC:$(K_{rel})_{I:pre}$		RSC:$(K_{rel})_{II:pre}$	
	Pre1 (CE-PTA)	Pre2 (CE-TPB)	$(K_{rel})_{I:pre1}$	$(K_{rel})_{I:pre2}$	$(K_{rel})_{II:pre1}$	$(K_{rel})_{II:pre2}$
Na^+	8.62×10^{-2}	1.39×10^{-3}	8.18×10^{-5}	5.07×10^{-3}	4.93×10^{-5}	3.06×10^{-3}
K^+	1.0×10^{-3}	2.65×10^{-3}	4.66×10^{-2}	1.75×10^{-2}	3.1×10^{-2}	1.18×10^{-2}
Ca^{++}	1.26×10^{-2}	4.28×10^{-2}	7.97×10^{-4}	2.34×10^{-4}	6.81×10^{-4}	2.0×10^{-4}
Mg^{++}	5.26×10^{-3}	2.34×10^{-3}	8.78×10^{-4}	1.97×10^{-3}	7.19×10^{-4}	1.61×10^{-3}
Glycine	1.96×10^{-3}	1.15×10^{-2}	1.01×10^{-3}	1.73×10^{-4}	6.62×10^{-4}	1.12×10^{-4}

Table (4): Determination of dopamine in pharmaceutical samples using the proposed electrode type-II.

Drug	Spectroscopic method[4]		Present method electrode-II		RSD*, %
	Found, mg/ml	Recovery, %	Found, mg/ml	Recovery, %	
Dopamine HCl injection (40ml/5ml), EIPICO, Egypt	0.77	100.1	0.79	98.6	1.32
Dopamine HCl injection (40ml/5ml), Ebewe Pharma, Austria	0.79	99.3	0.76	99.7	1.64
Dopamine HCl injection (40ml/5ml), Pierre Fabre, France	0.76	98.7	0.78	98.5	1.47

*) Relative standard deviation (four determinations)

The electrode was applied for determination of dopamine in banana. The results agreed with those obtained by the mentioned spectrophotometric method. Table 5 summarizes the obtained results for dopamine in banana pulp after 2 days ripening.

Table (5): Determination of dopamine in banana pulp samples after two days ripening using the proposed electrode type-II.

Sample	Spectroscopic method[4]	Present method electrode-II	
	Found, µg/ml	Found, µg/ml	RSD*, %
I	34.1	33.5	1.42
II	47.9	46.7	0. 83
III	65.4	68.2	1.61

*) Relative standard deviation (four determinations)

CONCLUSION

Application of originally formulated diazacrown ether derivative as a new ionophore for preparing dopamine electrode showed successful results. The selectivity and the sensitivity of the present electrodes based on the synthesized diazacrown ethers were found to be better than those for electrodes based on the non-aza crown ethers.

The use of the new concept of the relative selectivity coefficient is very useful in judgment between the different electrodes those are selective to the same ion. This made the comparison more accurate and specific.

REFERENCES

1- Benes FM: **Trends in Pharm. Scien.**; 22: 46-47 (2001).

2- Nalewajko E, Wiszowata A and Kojło A: **J. Pharm. and Biomed. Anal.**; 43: 1673-1681(2007).

3- Mamiński M, Olejniczak M and Chudy M et al.: **Anal. Chim. Acta**; 540: 153-157 (2005).

4- Abdulrahman LK, Al-Abachi A and Al-Qaissy MH: **Anal. Chim. Acta**; 538: 331-335 (2005).

5- Lai GS, Zhang HL and Jin CM: **Electroanal.**; 19: 496-501(2007).

6- Kooshki M and Shams E: **Anal. Chim. Acta**; 587: 110-115 (2007).

7- Alpat S, Alpat SK and Telefoncu A: **Anal. Bioanal. Chem.**; 383: 695-700 (2005).

8- Lin X and Gong J: **Anal. Chim. Acta**; 507: 259-265 (2004).

9- Hayashi K, Iwasaki Y and Kurita R et al.: **Electrochem. Comm.**; 5: 1037-1042 (2003).

10- Cheng Q, Peng TZ and Hu XB et al.: **Anal. Bioanal. Chem.**; 382: 80-4 (2005).

11- Sotomayor MDPT, Tanaka AA and Kubota LT: **Electrochim. Acta**; 48: 855-865 (2003).

ISSN 1110-5089

12- Tu YF and Chen HY: **Biosen. and Bioelect.**; 17: 19-24 (2002).
13- Mazzei F, Botre F and Lanzi M et al.: **Sens. and Actuat.**; 7: 427-430 (1992).
14- Saijo R, Murakami H and Tsunekawa S et al.: **Chem. Pharm. Bull.**; 55: 417-21 (2007).
15- Júnior LR, Fernandes JCB and de Oliveira Neto G et al.: **J.Electroanal. Chem.**; 481: 34-41(2000).
16- Othman AM, Rizka NM and El-Shahawi MS: **Anal. Sci.**; 20: 651-5 (2004).
17- Montenegro MC and Sales MG: **J. Pharm. Sci.**; 89: 876-84 (2000).
18- Lima JLFC and Montenegro MCBSM: **Mikrochim. Acta**; 131: 187-190 (1999).
19- Liu KY and Yu RQ: **Sci. China B.**; 33: 1466-80 (1990).
20- Romphophak T, Siriphanich J and Yoshinori U et al.: **Bull. Osaka Yuhigaok. Jun. Coll.**; 49: 17-21(2005).
21- Hodgkinson LC, Johnson MR and Leigh SJ et al.: **J. Chem. Soc. Perkin I**; 2193-2202 (1979).
22- Zareh MM, Malinowska E and Kasiura K: **Anal. Chim. Acta**; 447: 55-61 (2001).
23- Guilbault G, Drust R and Frant M et al.: **Pure Appl. Chem.**; 48: 127-132 (1976).
24- Rockville MD: Guidance for Industry Bioanalytical Method Validation, US Department of Health and Human Services, Food and Drug Administration: Center for Drug Evaluation and Research. www.fda.gov.com (2001).

Received: June 07, 2007
Accepted: July 18, 2007

معامل الاختيارية النسبية كمفهوم جديد لتقييم الحساسات الكهروكيميائية للدوبامين

محسن زارع

قسم الكيمياء – كلية العلوم – جامعة الزقازيق – الزقازيق 44519 – مصر

لقد تم ادراج نوعين من الحساسات الكهروكيميائية للتقدير الاختياري للدوبامين. فكلا من رباعي فلوروفينيل بورات البوتاسيوم(TFPB) و الداي ايثوكسي كربونيل10،1- ثناي ازو16،13،7،4- رباعي اوكسي سيكلو اوكتاديكان (DZCE) المخلق، تم استخدامهما كحامل للايون مشحون او متعادل. و قد كانت منحنيات المعايرة مرضية بالنسبة لميل نرنست في مدى خطي بين 9 $\times 10^{-3}$ الى 7.9×10^{-6} مولاري. و كان مدى الاس الهيدروجيني لهذه الاقطاب بين 3.5 و 8.3 . و تم حساب قيم معامل الاختيارية لعدد من الكاتيونات الغير عضوية و الاحماض الامينية و المركبات الصيدلية. و قد أدرج معامل الاختيارية النسبية و تم استخدامه لتقييم الخواص الاختيارية لاقطاب الدوبامين باستخدام معادلة- زارع. و قد تم تعريف و حساب متوسط معامل الاختيارية النسبية ، و المتوسط الكلي لمعامل الاختيارية النسبية لكل قطب. و قد لوحظ تحسن في الخواص الاختيارية عند اضافة DZCE كحامل متعادل في تركيب الغشاء. و قد استخدمت الاقطاب في تقدير الدوبامين في بعض المستحضرات الصيدلية.