ORIGINAL PAPER

A deuterium-palladium electrode as a new sensor in non-aqueous solutions: potentiometric titration of weak acids in *N*,*N*-dimethylformamide and *N*-methylpyrrolidone

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Received: 12 November 2008 / Revised: 23 January 2009 / Accepted: 26 January 2009 / Published online: 17 February 2009 © Springer-Verlag 2009

Abstract A deuterium-palladium electrode was employed as a new indicator electrode for the titration of weak acids in N.N-dimethylformamide and methylpyrrolidone. The investigated electrode showed a linear dynamic response for *p*-toluenesulfonic acid in the concentration range from 0.1 to 0.001 M, with a nernstian slope of 78.0 mV in N.Ndimethylformamide and of 64 mV per decade in Nmethylpyrrolidone. Sodium methylate, potassium hydroxide, and tetrabutylammonium hydroxide proved to be very suitable titrating agents for these titrations. The potential in the course of the titration and at the titration end point was rapidly established. The response time was less than 10-11 s, and the lifetime of the electrode is long. The experimental results obtained for the proposed electrochemical sensor and a conventional glass electrode were in good agreement. The advantages of the electrode are log-term stability, fast response, reproducibility, and easy preparation.

Keywords Potentiometry · Deuterium–palladium electrode · Sensor · Non-aqueous media

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Introduction

Weak acid or base, the acid dissociation constant of which is less than 10^{-7} , cannot be accurately titrated in aqueous solution. Usually, this problem can be solved partially or entirely using appropriate non-aqueous solvents as the reaction medium. Among non-aqueous solvents, N,Ndimethylformamide and methylpyrrolidone have been extensively used as media for the potentiometric determination of many acidic substances [1]. A glass electrode is most frequently used as the indicator electrode, both in aqueous and non-aqueous media. In an aqueous environment, glass electrodes are very popular due to their high selectivity and dynamic pH range. However, in spite of the distinctive potential characteristic of pH-glass electrodes and their use in routine pH measurements for many years, they have certain limitations [1]. In non-aqueous media, these electrodes show certain undesirable features: The potential response of a glass electrode in non-aqueous solution is often very slow. In some cases, it takes over 1 h before the equilibrium potential is attained. In addition, the electrodes have a limited useful life when employed in nonaqueous titrations because the solvents dehydrate the glass membrane, thereby reducing its affinity for, or response to, hydrogen ions.

These disadvantages of glass electrodes have led to an intensive search for alternative pH electrodes in nonaqueous solution. For this purpose, Lintner and others [2] used a platinum electrode for titration in tetrahydrofuran with lithium aluminum hydride. A platinum electrode was also used by Katz and Glenn [3] for titrations in ethylenediamine. Harlow et al. [4] used an anodically polarized platinum wire and antimony as an indicator electrode for the titration of very weak acids in some solvent. Greenhow and Al-Mudarris [5] used metal and metalloid indicator electrodes for the potentiometric titration of weak acids in dimethylformamide and 4-methyl-2-pentanone and Izutsu et al. [6-8] used silicone nitride (Si₃N₄), tantalum oxide (Ta₂O₅), and iridium oxide pH sensors in non-aqueous solution. However, redox interference is a known problem with metal oxide electrodes.

In previous studies, many deficiencies of the glass electrode (high resistance, fragility, contamination of the membrane, alkaline error, and dehydration of the glass membrane in non-aqueous media) were eliminated using natural monocrystalline pyrite, chalcopyrite, and galena as electrochemical sensors for the potentiometric titrations of weak acids in pyrrolidone, N,N-dimethylformamide, pyridine, γ -butyrolactone, propylene carbonate, acetonitrile, propionitrile, and benzonitrile [9–11].

However, the proposed electrodes cannot be applied in potentiometric titration in the solvents that dissolve the crystal holder. For such solvents, sensor carrier must be made of Teflon or some other material, which is not soluble in the investigated solvent.

Experiments by Fleishman and Pons [12] have stimulated activities in a large number of laboratories to study "cold fusion" phenomena and also inspired fundamental exploration of electrochemical behavior of palladium electrode. They also inspired us to examine the possibility of the analytical application of the deuterium–palladium electrode as a generator electrode in the coulometric–potentiometric determination of bases in propylene carbonate and ketone media [13,14] and as an indicator electrode for the potentiometric determination of acids and bases in water [15].

In this study, the possibility of applying D_2/Pd as a sensor (sensor carrier is palladium, the metal that is chemically inert in organic solvents) for the potentiometric determination of weak organic acids in *N*,*N*-dimethylforma-mide and methylpyrrolidone as solvents was investigated.

Experimental

Reagents

All the chemicals used in the present study were of analytical reagent from Merck, Fluka or Baker.

Deuterium oxide (99.8% pure, ZGN Chemical Radioiso-tope Division).

N,*N*-Dimethylformamide and *N*-methylpyrrolidone (Fluka) were puriss p.a. purity: *N*,*N*-dimethylformamide (\geq 99.8%) with a water content \leq 0.1%, methylpyrrolidone (\geq 99%) with a water content \leq 0.1%. These solvent were used without further purification. The water content in the applied solvents was controlled using Karl Fischer titration.

The preparation of the solutions of titrated acids, the solution of sodium methylate in the mixture of benzene and methanol, and the standard solutions of tetrabutylammonium hydroxide and potassium hydroxide was described in our previous paper [1].

p-Toluenesulfonic acid monohydrate was dried in vacuo over P_2O_5 at 70–80 °C for several days.

The Thymol Blue solution was prepared by dissolving 0.1 g of Thymol Blue in 100 mL of methanol.

The required volume of the acid was measured by means of a micro burette with a PTEF stopcock; 2.00–3.00 mL of the investigated acids was measured.

All measurements were carried out at room temperatures between 20 and 25°C.

Electrodes

The indicator D_2/Pd electrodes were made of conventional palladium wire (2 cm long, diameter being 0.5 or 1.0 mm). The wire was spiral-folded and sealed into a glass tube by means of platinum and connected with the pH meter using a contact made of copper wire.

The platinum used for the connection with the Pd wire was never exposed to the solution; hence, it did not have an effect upon the potentials measured. The prepared Pd electrode was heated in oxidation flame, and after that, the wire was saturated with gaseous deuterium, obtained by electrolyzing deuterium oxide at 1 mA electric current.

Cathode (Pd spiral):

$$D_2O + e^- \rightarrow D_{ads} + OD^-$$
 (1)

$$D_{ads} \rightarrow D_{(lattice Pd)}$$
 (2)

Anode (Pt spiral):

$$D_2O \rightarrow 2D^+ + 1/2O_2 + e^-$$
 (3)

Since anolyte is not separated from catholyte, during electrolysis of deuterium oxide, deuterium is obtained on the cathode and oxygen on the anode:

$$2D_2O \to 2D_2 + O_2 \tag{4}$$

Electrolysis of deuterium oxide was performed without the addition of supporting electrolyte because the voltage of electrolysis was small at this current strength. The electrode was loaded with deuterium as long as the bubbles of deuterium portioned on the surface of palladium (cathode).

The response of the indicator D_2/Pd electrode in N, N-dimethylformamide and N-methylpyrrolidone was compared with that of a conventional glass electrode, type

G-202C (Radiometer, Copenhagen). The glass electrode was conditioned in the appropriate solvent before use.

The reference electrode was a modified KCl saturated calomel electrode (SCE). The modification of the SCE electrode of the type 401 (Radiometer, Copenhagen) was made by the complete replacement of its inner solution with a methanolic potassium chloride solution. The solution was vigorously stirred with a magnetic stirrer during the titration.

Apparatus

The apparatus employed to follow the potential changes of the D_2/Pd electrode with time and for end-point detection with either a D_2/Pd electrode-SCE or a glass electrode-SCE couple is show in our previous paper [10]. The potential changes during the titration were followed with a Digital 870 pH meter, Dresden.

The same apparatus with an additional temperaturecontrolled cell was used to follow the potential changes of the employed electrode as a function of the concentration of p-toluenesulfonic acid.

Procedure

Potential measurement

The stationary potential measurements of the D_2/Pd electrode were performed in a series of *p*-toluenesulfonic acid in the concentration range of 0.1–0.001 M. The potential of the D_2/Pd electrode with time was followed in a temperature-controlled cell (25 ± 0.1 °C). The ionic strength of the solution was maintained with 0.05 M tetrabutyl ammonium perchlorate. The potential values determined in this way were used to calculate the slopes.

The change the potential of the D_2/Pd electrode with time was followed in the required solvent. This indicator electrode was coupled to a modified SCE as the reference electrode.

The titration procedure was described in our previous paper [1].

Results and discussion

Mechanism

The palladium–deuterium electrode (denoted here as D_2/Pd [13,14,16]), as well as a H_2/Pd electrode [17,18], is very similar to a hydrogen electrode (with platinum). But, palladium has one significant feature, i.e., the capability to absorb (dissolve into itself) molecular hydrogen and deuterium.

Two phases (the alpha and beta phases, α -Pd and β -Pd) can co-exist in palladium when hydrogen or deuterium is absorbed:

1. The alpha phase exists at hydrogen concentrations <0.3 at.% (~0.03 H/Pd atomic ratio) [19]

 $\alpha - \mathrm{Pd} \rightleftharpoons \beta - \mathrm{Pd}$ transition

2. The beta phase exists when the ratio H to Pd=0.73 and D to Pd=0.70 [20], respectively.

The palladium-hydrogen electrode acts as a reversible hydrogen electrode:

$$2\mathrm{H}^+ + 2\mathrm{e} \to \mathrm{H}_2(\mathrm{g}) \tag{5}$$

The potential of this electrode is determined by the expression:

$$E_{\rm H} = E_{\rm H}^0 + 0.05916 \, \log a_{\rm H^+} \tag{6}$$

When palladium is electrochemically exchanged by deuterium, the potential of this electrode (as in the case of Pd/H_2) is given by the expression

$$E_{\rm D} = E_{\rm D}^0 + 0.05916 \, \log a_{\rm H^+} \tag{7}$$

where [21]

$$E_{\rm D}^0 = 4.31 \,\mathrm{mV}$$
 (8)

Hydrogen and deuterium dissolved in palladium can be desorbed from the electrode:

$$2D_{abs} \rightarrow 2D_{ads} \rightarrow D_2$$
 (9)

This recombination reaction proceeds following a diffusion of deuterium from the bulk of the metal to the electrode surface. The procedure of removal of hydrogen (deuterium) from palladium can be achieved electrochemically and non-electrochemically. Hydrogen (deuterium) dissolved in palladium can be chemically oxidized to $H^+(D^+)$ ions [13–18]. Chemical oxidation of hydrogen and deuterium can be performed using various oxidation means such as iodine, potassium-permanganate, cerium-sulfate, and oxygen [22]. Oxidation of hydrogen with oxygen is very slow and is carried out with difficulties if no water is present in palladium. Long induction period is necessary for the oxidation of hydrogen using atmospheric oxygen.

The potential of H₂/Pd electrode depends on the contents of hydrogen in palladium. At the beginning of filling, the potential of the electrode has a positive value (the zone before alpha phase). In the zone of the α -Pd/ β -Pd transition, the potential is very stable, and it has constant value of approx. +50 mV vs. reversible hydrogen electrode [23]. This potential is independent of the amount of hydrogen over a wide range. In the zone of the α -Pd/ β -Pd transition, the potential of deuterium electrode is also stable and is different from palladium–hydrogen electrode for a couple of millivolts. This property has been utilized in the construction of a palladium–deuterium indicator electrode.

From expression 7, it can be seen that the potential of D_2/Pd electrode depends (in water) on the activity of H_3O^+ ions. Equation 7 can also be applied in non-aqueous solvents containing weak organic acids.

Characteristics of a D₂/Pd electrode

If an ISE is to be applied as a sensor for quantitative measurements in a non-aqueous environment, the following conditions should be fulfilled: a stable potential in acid and base medium, a sufficient slope, sensitive, short response time and long-stability (lifetime), and repeatability.

Potential of the electrode

The stationary potential of the D₂/Pd electrode in *N*,*N*-dimethylformamide and *N*-methylpyrrolidone was measured by direct potentiometry at 25 ± 0.1 °C in a freshly prepared 0.05 M solution of *p*-toluenesulfonic acid in an appropriate solvent. All measurements were performed in the presence of a background electrolyte of constant ionic strength (0.05 M tetrabutylammonium perchlorate). In all the investigated solutions, a stable potential was attained in less than 3–5 min.

Slope of the potential response of a D₂/Pd electrode

The potential of the D₂/Pd electrode was determined using a series of various concentrations of *p*-toluenesulfonic acid in the range of 0.1–0.001 M in *N*,*N*-dimethylformamide and *N*-methylpyrrolidone in a temperature-controlled cell ($25\pm$ 0.1 °C). The ionic strength of the solutions was maintained with 0.05 M tetrabutylammonium perchlorate. The values of the slope of the potential in *N*,*N*-dimethylformamide was 78 mV and in *N*-methylpyrrolidone 64 mV for a given range of concentrations (Fig. 1). Since the D₂/Pd electrode exhibits super-Nernst dependences, it cannot be used for measuring the pH of a solution, but since the potential of a D₂/Pd electrode as an indicator electrode is very stable with respect to time, it can be successfully applied to the titration of acids in *N*,*N*-dimethylformamide and *N*methylpyrrolidone as solvent.

Response time of the electrode

The response time of the D_2/Pd electrode was determined by recording the elapsed time before the attainment of a stable potential value after the D_2/Pd electrode, and the reference electrode (modified SCE) was immersed in



Fig. 1 Plots of the D_2/Pd electrode potential vs. log c (*p*-toluene-sulfonic acid) in methylpyrrolidone

calibration solutions from highly acidic (0.05 M of *p*toluenesulfonic acid) to highly basic (0.05 M tetrabutylammonium hydroxide or 0.05 M KOH) solutions. The change of the electrode potential from the acidic (*p*-toluenesulfonic acid) to the basic region (tetrabutylammonium hydroxide (TBAH)) ranged from +483 to -473 mV (*N*-methylpyrrolidone), and from the acidic (*p*-toluenesulfonic acid) to basic region (KOH), it ranged from +267 to -279 mV (*N*,*N*-dimethylformamide). The response time was 10 s for *N*,*N*-dimethylformamide and 11 s for *N*-methylpyrrolidone. These results were within the limit of those obtained by many hydrogen electrodes giving a linear response time of the prepared D₂/Pd electrode was compatible with most similar electrodes reported in the literature [1,24,25].

Long-term stability (lifetime) and repeatability

The lifetime of the electrode was determined by raising the potential values of the calibration solution (*p*-toluenesulfonic acid) and plotting the calibration curves for a period of several years. The slope of the electrode remained the same. When the electrode is not used for the titration, it is kept in a dry place protected from dust. However, if the electrode was used frequently and for a long time, it was necessary to refill the D_2 /Pd electrode with deuterium by electrolysis, and to wash, dry, and continue with use.

In order to establish the efficiency of use of the D_2/Pd electrode in potentiometric titrations and the repeatability of the results obtained, the titration of benzoic acid with sodium methylate was selected as a model, and it was repetitively carried out for five times, and the end point was

Fig. 2 Five titration curves for 2 mL benzoic acid solution (~0.05 M), by standard sodium methylate solution of 0.05 M, using D_2/Pd as an indicator electrode in *N*.*N*-dimethylformamide



V/ mL (1 division = 0,1 mL)

monitored by using this electrode. The results obtained for the titration of benzoic acid with sodium methylate were shown in Fig. 2. The relative standard deviation (RSD) for the end-point determination of titration was found to be 0.28%. The values of RSD for the end-point determination of titrations of different acids are shown in Table 2.

Analytical application

The practical utility of the proposed sensor was tested by its use as an indicator electrode for the titration of weak acids of different strengths, such as benzoic, anthranilic, stearic,



Fig. 3 The effect of the indicator electrode on the shape of the endpoint inflexion in the potentiometric titration of benzoic acid (*a*) and α -nitroso- β -naphthol (*b*) in *N*,*N*-dimethylformamide—*1a*, *3a*, *5a*, *1b*, *3b*, *5b*: D₂/Pd electrode; *2a*, *4a*, *6a*, *2b*, *4b*, *6b*: glass electrode. Titrant—*1a*, *2a*, *1b*, *2b*: sodium methylate; *3a*, *4a*, *3b*, *4b*: KOH; *5a*, *6a*, *5b*, *6b*: TBAH

and α -nitroso- β -naphthol, with methanolic potassium hydroxide, TBAH, and sodium methylate solution.

The titrations of acids in non-aqueous solvents with tetrabutylamonium hydroxide, potassium hydroxide, and sodium methylate were described in our previous papers [9,10].

The titration curves of benzoic acid and α -nitroso- β naphthol in *N*,*N*-dimethylformamide as the solvent are shown in Fig. 3. While titrating benzoic acid, for example, the potential jump at the titration end point (TEP) was 306 mV/0.3 mL in *N*-methylpyrrolidone and 289 mV/ 0.3 mL in *N*,*N*-dimethylformamide when a D₂/Pd electrode was used as the sensor. When benzoic acid was titrated with KOH and TBAH in the same solvents, the potential jumps were somewhat lower (with KOH 274 mV/0.3 mL



Fig. 4 Potentiometric titration curves of stearic acid in N,N-dimethylformamide obtained by using a D₂/Pd as indicator electrode and KOH as the titrant: (1) non-aqueous media, (2) 0.1%, (3) 1.0%, (4) 5.0%, and (5) 10.0% water

Table 1Potential jumps (mV/0.3 mL) at the end point in the
potentiometric titration of weak
acids in non-aqueous media

Solution	Titratedcompound	Titrating agent	D ₂ /Pd-SCE	Glass-SCE
N,N-Dimethylformamide	Benzoic acid Sodium methylate		289	91
	Benzoic acid	Potassium hydroxide	266	310
	Benzoic acid	TBAH	183	325
	Stearic acid	Potassium hydroxide	232	284
	Stearic acid	TBAH	216	225
	Anthranylic acid	Sodium methylate	315	-
	Anthranylic acid	Potassium hydroxide	251	-
	α -Nitroso- β -Naphtol	Sodium methylate	259	86
	α -Nitroso- β -Naphtol	Potassium hydroxide	174	262
	α -Nitroso- β -Naphtol	TBAH	171	219
<i>N</i> -Methylpyrrolidone	Benzoic acid	Sodium methylate	306	124
	Benzoic acid	Potassium hydroxide	274	331
	Benzoic acid	TBAH	205	308
	α -Nitroso- β -Naphtol	Sodium methylate	120	60
	α -Nitroso- β -Naphtol	Potassium hydroxide	176	277
	α -Nitroso- β -Naphtol	TBAH	128	216

in *N*-methylpyrrolidone and 266 mV/0.3 mL in *N*, *N*-dimethylformamide, with TBAH 205 mV/0.3 mL in *N*-methylpyrrolidone and 183 mV/0.3 mL in *N*,*N*dimethylformamide). In the titration of benzoic acid using a glass electrode as the indicator, the potential jump at the TEP with KOH and TBAH as the titrants amounted to about 300 mV/0.3 mL in both *N*-methylpyrrolidone and *N*, *N*-dimethylformamide (Table 1).

When a glass electrode was used for TEP detection, the potential jumps were decreased (124 mV/0.3 mL in *N*-methylpyrrolidone and 91 mV/0.3 mL in *N*,*N*-dimethylformamide) and were hardly perceptible when sodium

Table 2 Potentiometric titration of acids in N,N-dimethylformamide and N-methylpyrrolidone by the application of the electrode pairs D_2/Pd -SCE and glass-SCE

Titrated acid	Solvent	No. of determ	Taken (mg)	Found (%)	
				Glass-SCE	D ₂ /Pd-SCE
Benzoic acid	N-methylpyrrolidone	6	24.40	99.80±0.10	$99.85 {\pm} 0.20^{a}$
Benzoic acid	N-Methylpyrrolidone	6	24.40	100.11 ± 0.22	$100.20 {\pm} 0.15^{b}$
Benzoic acid	N-Methylpyrrolidone	5	24.40	$99.78 {\pm} 0.30$	$99.80 {\pm} 0.32^{\circ}$
α -Nitroso- β -naphthol	N-Methylpyrrolidone	6	53.50	98.78 ± 0.32	$98.99 {\pm} 0.52^{a}$
α -Nitroso- β -naphthol	N-Methylpyrrolidone	7	53.50	97.47±0.24	$97.51 {\pm} 0.35^{b}$
α -Nitroso- β -naphthol	N-Methylpyrrolidone	5	53.50	98.60 ± 0.20	$98.20 \pm 0.31^{\circ}$
Benzoic acid	N,N-Dimethylformamide	6	23.09	$99.85 {\pm} 0.40$	$99.82{\pm}0.26^{a}$
Benzoic acid	N,N-Dimethylformamide	5	23.09	99.86±0.25	$99.95 {\pm} 0.33^{b}$
Benzoic acid	N,N-dimethylformamide	6	23.09	$100.10 {\pm} 0.30$	$99.80 {\pm} 0.28^{\circ}$
α -Nitroso- β -naphthol	N,N-Dimethylformamide	7	44.48	98.00 ± 0.35	$98.30 {\pm} 0.40^{b}$
α -Nitroso- β -naphthol	N,N-Dimethylformamide	6	44.48	98.20±0.42	$98.12 \pm 0.34^{\circ}$
α -Nitroso- β -naphthol	N,N-Dimethylformamide	7	44.48	97.95±0.31	$98.28{\pm}0.28^{\rm b}$
Stearic acid	N,N-Dimethylformamide	5	55.02	$97.85 {\pm} 0.27$	$97.60 {\pm} 0.34^{\circ}$
Stearic acid	N,N-Dimethylformamide	7	55.02	97.66±0.11	$97.80 {\pm} 0.13^{a}$
Anthranylic acid	N,N-Dimethylformamide	6	24.40	99.40±0.35	$99.60 {\pm} 0.27^{\circ}$
Anthranylic acid	N,N-Dimethylformamide	6	24.40	99.55±0.32	$99.51 {\pm} 0.30^{a}$

^a Sodium methylate

^b Potassium hydroxide

^c TBAH

methylate was applied as the titrant due to the effect of sodium ions on the glass electrode.

While titrating α -nitroso- β -naphthol (weak acids, p K_a in water of 7.77) with D₂/Pd as the sensor, high potential jumps were obtained in the titration with sodium methylate (120 mV/0.3 mL in *N*-methylpyrrolidone and 259 mV/0.3 mL in *N*,*N*-dimethylformamide). Sufficiently high potential jumps in *N*-methylpyrrolidone and *N*,*N*-dimethylformamide were also obtained with the other two titrants (with KOH 176 mV/0.3 mL in *N*-methylpyrrolidone and 174 mV/0.3 mL in *N*,*N*-dimethylformamide, and with TBAH 128 mV/0.3 mL in *N*-methylpyrrolidone and 171 mV/0.3 mL in *N*,*N*-dimethylformamide).

When the D_2/Pd electrode was applied as the indicator electrode in *N*,*N*-dimethylformamide and *N*-methylpyrrolidone as solvent, the potentials during the titration and at the equivalence point (TEP) were rapidly established (within a couple of minutes), and the change of the potential at the TEP coincided with that of the applied indicator color.

Water lowers the potential jumps at the TEP in all the applied solvents. The stearic acid titration curves in N, N-dimethylformamide at different concentrations of water are shown in Fig. 4. A more significant decrease of the potential jump was obtained when the content of water was increased by 10%. The impact of water on the decrease of the potential was much stronger in the titrations of very weak acids. Since water is released during the titration of acids when applying TBAH and KOH [9,10], it is best to use sodium methylate as the titrant.

The results obtained in the determination of the investigated acids (Table 2) in the investigated solvents using a D_2/Pd indicator electrode deviated on average by $\pm 0.02-0.40\%$ in relation to those obtained with a glass electrode.

Our further investigations have shown that D_2/Pd electrode is an excellent sensor for potentiometric titrations of weak acids in nitriles, ketones, alcoholes, γ -butyrolactone, propylene carbonate, and tetrahydrofuran as solvents.

Conclusion

The obtained results show that a D_2/Pd electrode can be successfully applied as the indicator electrode for the titration of weak acids in *N*,*N*-dimethylformamide and *N*methylpyrrolidone, with standard base solutions (potassium hydrohide, sodium methylate, and TBAH). The potential during the titration and at the equivalence point (TEP) were rapidly established, and the change of the potential at the TEP coincided with the change of the color of the applied indicator. The sensor carrier is palladium, the metal that is chemically inert in all working mediums, so this electrode is very suitable for such determinations. Therefore, the proposed electrode can be a good alternative for a glass electrode in the investigated solvents.

Acknowledgment This work was funded by the Ministry of Science of the Republic of Serbia (Project No. 142060 B).

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