

Synthesis, Biocidal and Analytical Applications of Some Novel 1-Acyl / benzoyl -1-anilido-4-methyl-aryl-butadiene Derivatives

M. S. T. Makk*, R. M. Abdel-Rahman and M. S. El-Shahawi

Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia

Abstract

The present investigation was aimed to synthesis a series of new 1-acyl/ benzoyl -1-anilido-4-methyl - aryl-1,3-butadiene derivatives (II-IV) for their uses as biocidal and analytical reagents. The compounds were prepared by warming 4-aminoantipyrine, 2-amino-5-chloropyridine, 2-amino-5-nitropyridine, 2-aminobenzthiazole, sulfanilamide and/ or sulfadiazine with pre heated ethyl acetoacetate and/ or ethyl benzoylacetate in dry conditions followed by condensation with crotonaldehyde and/or 4-dimethylaminocinnamaldehyde in boiling ethanol-piperidine. The compounds were fully characterized via their elemental analysis and spectroscopic measurements (UV Vis., IR, NMR). The biocidal effects of the prepared compounds (III d, e, f, IV d, e, f) as antimicrobial agents and photochemical probe agents was investigated. The voltammetric behavior of the two compounds IIa and IVa in N,N-dimethylformamide was investigated. The compound IVa was successfully tested for the removal and / or separation of bismuth (III) employing polyurethane foam solid sorbent.

Keywords: Synthesis; 1-Acyl/ benzoyl -1-anilido-4-methyl - aryl-1, 3-butadiene; Biocidal voltammetry; Wastewater

Introduction

Recent years have seen an upsurge of interest on the synthesis and spectroscopic characterization of β - diketones as potential ligands [1,2]. Complex formation in this class of compounds is conceived by replacement of the enolic proton by chelation with metal ions in a bidentate fashion [3,4]. The β - diketone 3- salicylidene-2, 4-pentanediones and related compounds have been used successfully as proper chelating agents with a series of many metal ions [5,6,7]. Knoevenagel condensate of substituted benzylidenes with active methylene compounds were performed efficiently employing ultra stable Zeolite as heterogeneous catalyst [8-11] have reported a series of benzoyl -acetanilides and their physico organic properties. The starting material was used by Abdel-Rahman [11] for building a series of novel bio- active pyrazoline derivatives. In addition, the thermodynamic characteristics and spectroscopic characterization of a series of compounds namely hydrazono - 1, 3- bi carbonyl derivatives and their lanthanide complexes have been investigated [9,10].

The chelation behavior of a series of dicarbonyl towards some metal ions has been reported [12-14]. Moreover, metal chelates of β - diones have interesting properties in particular in industrial applications [15-17]. The dimerized species of 2- diazo-3- methyl-1-phenyl-5-pyrazolone produced the compound 4- (5-hydroxy-4-pyrazolxlimino-2-pyrazolin-5- one. Such investigations have indicated that, no work is known on the Knoevenagel condensate β - ketoanilide and its metal chelates. Therefore, in continuation to our previous work [18-23], the present study is focused on the synthesis and characterization of a series of some -diketone derivatives bearing anilido moieties and their unsaturated -diketone derivatives. In view of the voltammetric behavior, one of the prepared compounds was successfully tested as a trapping agent for the pre-concentration of bismuth (III) from aqueous as a highly toxic metal ions the industrial waste water.

Experimental

Reagents and materials

Low density polyethylene (LDPE) bottles, Nalgene were carefully cleaned first with hot detergent, soaked in 50% HCl (Analar), HNO₃

(2.0 mol L⁻¹), subsequently washed with dilute HCl (0.5 mol L⁻¹) and finally rinsed with distilled water. N,N-Dimethylformamide (DMF) and the supporting electrolyte tetraethyl ammonium chloride (TMA⁺. Cl⁻) were purchased from BDH chemicals.. The sample solution was stored in LDPE bottles and stored at -20°C. Britton - Robinson (B -R) buffers of pH 2-11 were prepared from the acid mixture of phosphoric acid, boric acid, acetic acid (0.04 mol L⁻¹) and adjusting the pH to the required value with sodium hydroxide (0.20 mol L⁻¹). A stock BDH stock solution of bismuth (1 mg/mL) in dilute nitric acid was used. A series of standard diluted bismuth (III) solutions were then prepared in doubly distilled water by dilution. Stock solutions (1×10⁻² mol L⁻¹) of the compounds -acyl-1-anilido-4- methyl-1,3- butadiene, IIa and 1-benzoyl-1-anilido-4- methyl-1,3- butadiene, IVa in DMF were prepared. The supporting electrolyte tetra methylammonium chloride (TMA⁺.Cl⁻) was used in the voltammetric experiments as received without further purifications.

Apparatus and measurements

A Perkin Elmer (Lambda EZ-210) double beam spectrophotometer (190-1100 nm) with 1cm (path width) was used for recording the electronic spectra of the prepared solutions. Digital pH-meter (model MP220, Metter Toledo) was used for pH measurements. A Perkins Elmer model RXI-FT-IR system 55529 was used for recording the IR spectra of the prepared compounds. A Bruker advance DPX 400 MHz model using TMS as an internal standard was used for recording the ¹HNMR spectra of the compounds on deuterated DMSO. A GC-MS-QP 1000-Ex model was used for recording the mass spectra of the compounds. Melting points were determined with an electro thermal Bibbly Stuart Scientific Melting Point SMPI (US). Molecular weights

*Corresponding author: MST Makk, Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 80203, Jeddah 21589, Kingdom of Saudi Arabia, E-mail: mmakki@kaau.edu.sa

Received December 22, 2009; Published October 31, 2012

Citation: Makk MST, Abdel-Rahman RM, El-Shahawi MS (2012) Synthesis, Biocidal and Analytical Applications of Some Novel 1- Acyl / benzoyl -1- anilido-4- methyl-aryl-butadiene Derivatives. 1:443. doi:[10.4172/scientificreports.443](http://dx.doi.org/10.4172/scientificreports.443)

Copyright: © 2012 Makk MST, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

of the compounds were preformed on Micro analytical center, Cairo University, Egypt. Microanalysis (Nitrogen %) was performed by microanalytical center Ain-Shams University-Cairo-Egypt. A Metrohm 797 VA trace analyzer and 797 VA stand were used for recording the cyclic voltammetric (CV) experiments. In the CV experiments, a three-compartment (Metrohm) voltammetric cell (10 mL) incorporating Pt wire as working, double-junction Ag/AgCl,(3M KCl), as reference and Pt wire (BAS model MW-1032) as counter electrodes, respectively. The surface area of the counter electrode was 100 times larger than the area of the working electrode.

Methodology

Preparation of acyl/benzoyl acetanilide Derivatives (I and III): To preheated ethyl acetoacetate and/or ethylbenzylacetate (0.01mol) a selective hetero primary amines and/or sulfa drugs (0.01mol) were added in dry system then warmed for 10-15 min at 100-110°C, cooled and finally washed with diethyl ether. The resultant solid was dried and crystallized to give I and III respectively (Table 1).

Formation of 1-acyl/benzoyl-1-anilido-4-methyl/aryl-1,3-butadiene (II and IV): Equimolar mixture of compounds I and/or III and unsaturated aldehydes as crotonaldehyde and/or 4-dimethylaminocinnamaldehyde in absolute ethanol (100 mL), piperidine (0.5 mL) was heated under reflux for 8 h, cooled. The solvent was removed and the obtained solid was crystallized to give II and IV respectively (Table 1).

Preparation of the reagent IVa immobilized polyurethane foam packed column: Polyurethane foam (PUFs) cubes immobilized with the reagent IVa were prepared by mixing the dried foam cubes with the required weight of the reagent (0.05% w/v) in ethanol with efficient stirring for 10 min. The reagent immobilized PUF cubes were then dried to remove the excess reagent with filter papers as reported earlier [19-21]. The reagent immobilized PUFs were packed separately in the glass columns by applying the vacuum method of foams packing.

Pre concentration and/ or separation of bismuth (III) by reagent IVa treated PUFs: An accurate weight (0.1 ± 0.01 g) of the reagent IVa treated foam cubes was equilibrated with 50 mL of an aqueous solution containing bismuth (III) ions at concentration of 10 µg mL⁻¹. The solutions were then adjusted to the required pH with B-R buffer

(pH 2-11). The test solutions were then shaken for 2 h on a mechanical shaker. The aqueous phase was then separated out by decantation and the amount of bismuth (III) remained in the aqueous phase was determined with atomic absorption spectrometry at the optimum wavelength. The amount of bismuth (III) retained on the PUFs cubes was determined from the difference between the concentration of bismuth (III) solution before (Co) and after (Ca) shaking with the foam cubes.

Results and Discussion

Spectroscopic characterization

Synthesis of 1, 3-dicarbonyl anilido and their unsaturated derivatives is very simple and of general applicability. It gives pure compounds with improved yields. Thus, warming some hetero primary amines such as 4-aminoantipyrine, 2-amino-5-chloropyridine, 2-amino-5-nitropyridine, 2-amiobenzthiazole and some sulfa drugs as sulfanilamide and sulfadiazine with preheated ethyl acetoacetate and/or ethyl/benzoyl acetate at 100-110°C for 10-15 min in dry condition led to the formation of acyl/benzoyl acetanilide derivatives I and III (Scheme I, II). Knoevenagel condensation of compounds I and III with unsaturated aldehydes such as crotonaldehyde and/or 4-dimethylcinnamaldehyde in boiling ethanol with few drops of piperidine as catalyst afforded 1-acyl/benzoyl -1-anilido-4-methyl-1,3 butadiene (II) and 1-acyl/benzoyl-1-anilido-4-(4'-dimethylaminophenyl)-1,3-butadiene (IV) respectively (Scheme 1-III). Both carbonyl compounds I-IV having a second carbonyl at -position, are termed as -diketones. In general hydrogen bonding is possible only in syn form and not in anti form, where the orientation of enolization is towards the aryl or phenyl groups [5] indicating the high enolic content of 4-aryl-1, 3-diketones and not in 4-methyl-1, 3-diketones. UV – Visible spectra of compounds II and IV have two strong bands around 360 and 260 nm which characteristics bands of carbonyl chromophore and the conjugated C=C of butadiene (n-* and *transition) while that of compounds I and III recorded a low bands at 330 and 240 nm due to a bathochromic shift, indicating the involvement of the two carbonyl groups isolated by methylene group, assigned to the intramolecular charge transfer interaction involving the whole molecule [6]. IR spectra of compounds

Compd No.	M.P. (°C)	Yield (%)	Solvent	M. Formula	M. Weight		N analysis*	
					Found	Calcd	Found	Calcd
Ia	130	80	Pet. ether 60-80	C ₁₅ H ₁₇ N ₃ O ₃	283	287	13.10	14.63
Ib	165	70	Pet. ether 60-80	C ₉ H ₉ N ₂ ClO ₂	209	212	13.42	13.20
Ic	158	75	Pet. ether 60-80	C ₉ H ₉ N ₃ O ₄	219	223	17.73	18.81
Id	225	75	Pet. ether 60-80	C ₁₁ H ₁₀ N ₂ SO ₂	230	234	11.52	11.96
Ie	135	80	Pet. ether 60-80	C ₁₀ H ₁₂ N ₂ SO ₄	251	256	9.99	10.93
If	210	85	Pet. ether 60-80	C ₁₄ H ₁₄ N ₄ SO ₄	330	334	16.64	16.76
Ila	150	72	THF	C ₂₀ H ₂₀ N ₄ O ₄	373	380	14.61	14.73
Ilb	170	75	THF	C ₁₅ H ₁₄ N ₂ SO ₂	281	286	8.85	9.79
IIla	140	73	Pet. Ether 100-140	C ₂₀ H ₁₉ N ₃ O ₃	343	349	11.21	12.03
IIlb	170	78	Pet. Ether 100-140	C ₁₄ H ₁₁ N ₂ ClO ₂	270	275	9.51	10.18
IIlc	162	80	Pet. Ether 100-140	C ₁₄ H ₁₁ N ₃ O ₄	279	285	13.7	14.73
IIld	300	90	Pet. Ether 100-140	C ₁₆ H ₁₂ N ₂ SO ₂	290	296	8.55	9.45
IIle	240	85	Pet. Ether 100-140	C ₁₅ H ₁₄ N ₂ SO ₄	312	318	7.90	8.80
IIlf	335	82	Pet. Ether 100-140	C ₁₉ H ₁₆ N ₄ O ₄	388	396	12.93	14.14
IVa	125	70	Diethyl ether	C ₂₅ H ₂₂ N ₄ O ₄	433	442	12.2	12.66
IVb	280	72	Diethyl ether	C ₂₀ H ₁₆ N ₂ SO ₂	341	348	7.1	8.04
IVc	140	60	Diethyl ether	C ₂₇ H ₂₃ N ₃ SO ₂	443	453	8.5	9.27

* All the prepared compounds gave analytical C and H data with ± 0.4-0.7% from the theoretical values.

Table 1: Physical properties of prepared compounds I-IV

Compound 50 mg/mL	Bacteria Escherichia coli	Fungi Asperigillus fumigates	Bacteria Escherichia coli	Fungi Asperigillus fumigates
IIIId	15	17	18	22
e	20	22	25	24
f	25	21	27	27
IVd	13	12	14	14
e	12	10	15	15
f	14	14	17	18

* Highly active >20; moderate (15 – 20) and weak < 15.

Table 2: The Biocidal and photochemical Effects of Some Compounds.

I and III show no characteristic C=O absorption band (at 1725-1710 cm^{-1}) which is present in the spectrum of acetylacetone $\sim 1680 \text{ cm}^{-1}$ while that of II and IV recorded of strong absorption bands at 1650 cm^{-1} of true C=O group. Also, intramolecular as well as intermolecular hydrogen bonding are observed in the regions 2700-2500 and 3000-2900 cm^{-1} respectively. The presence of absorption bands at 1610-1480 cm^{-1} (C=C) and 960-900 cm^{-1} confirm the presence of trans -CH=CH- moiety of compounds II and IV respectively. These vibrations indicate that the transformation of the electronic effect is quite apparent through the part comprising the NH, OH and CO groups.

¹HMR spectra of compounds I and III showed a one proton signal at ~ 15 ppm which confirm the presence of strong intramolecular hydrogen bonded enol proton, in addition, a signal appeared at 6.5-6.8 (methine) 6.9-7.9 ppm (aryl)protons. In such systems, the maximum enolization is two especially if containing aryl moieties. On the other hand, ¹HMR spectra of compounds II and IV, showed a resonance signals at 8.0-8.5 ppm (olefinic), 2.5 ppm (methyl protons (due to an allylic coupling between HC=CH and methyl group), in addition of aromatic protons at δ 6.7-7.7 ppm. Also, the tautomeric forms of compounds I and III is evidence by PMR which showed one resonated singlet for proton linked to sp^3 -carbon at 4.66 ppm. Moreover, structures of the compound Id and IIIId were deduced from ¹³C NMR, Id recorded δ at 29.9 (CH_3), 202.8 (C=O), 51.7 (CH_2), 164 (b C=O), 174.5 (S-C=N), 153, 130 (C_4 & C_5 of thiazole) and 118 -121.8 ppm (benzocarbons); while compound IIIId showed δ at 194.2 (C=O), 117 (HO-C=C), 66 (CH=C-OH), 174.5 (S-C=N), 153, 130.8 (C_4 & C_5 of thiazole) and 118.3 -122.8, 136 -128 ppm (benzo and phenyl protons). According to the ¹H and ¹³C NMR data, the acyl/benzoyl anilide derivatives have mainly an enolic structure with intra molecular hydrogen bonding in solution state, while the styryl of acyl/benzoyl anilides exist predominantly in the cis- form established by some type of interaction.

Mass spectroscopy of compounds I-IV give another indication of their stability which shown the degree between ketonic and enolic equilibrium. Also, fragmentation results give us a different ways between Me-CO and Ar-CO structures. A good physico chemical evidence for the presence of enolic and or ketonic tautomers of compounds I and III was deduced from free solubility of their Ar-NHCO derivatives in aqueous NaOH which confirm that the enolization forms take place towards aryl and or phenyl groups [5].

Biocidal effect

Some synthesized compounds were tested *in-vitro* using the agar diffusion disk method [20,21]. [The antimicrobial potentialities of the test compounds were estimated by placing pre sterilized filter paper disks (11 mm diameter) impregnated with 50 mg/disk using DMSO as solvent, which showed no inhibition zone (IZ) of tested compounds (mm) were measured after 24h incubation at 37°C for bacteria and after 5-days incubation at 28°C for fungi (Table 2). Photochemical probe effects of these compounds can be determined using UV – 360 as

second test. Compounds IIIe,d,f and IVe,d,f showed a highly biocidal effect and only compound IIIe,d,f characterized by photochemical probe action than other prepared compounds.

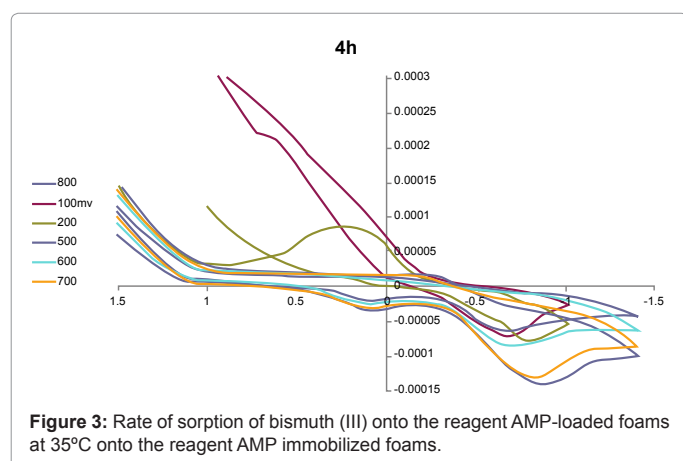
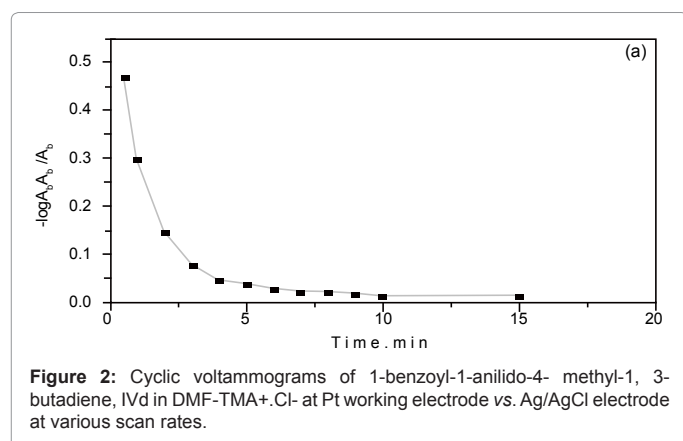
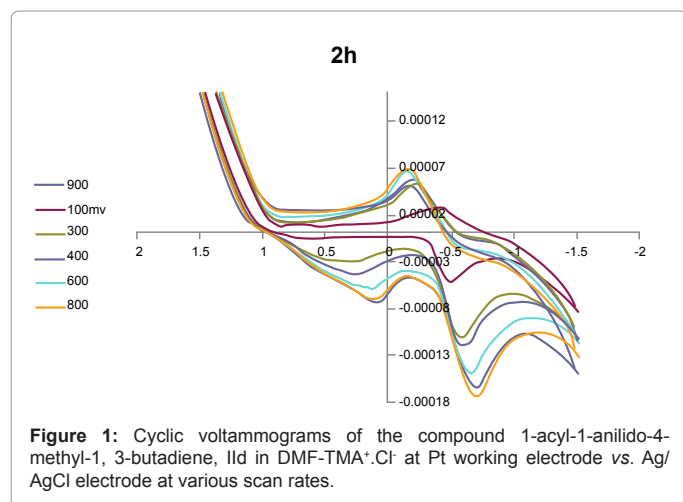
Voltammetric study

The cyclic voltammograms (CVs) of the two compounds 1-acyl-1-anilido-4- methyl-1,3- butadiene, IIa and 1-benzoyl-1-anilido-4-methyl-1,3- butadiene, IVa in DMF - TMA⁺.Cl⁻ at Pt working electrode versus Ag/AgCl reference electrode at various scan rate were investigated. The results are shown in Figures 1 and 2. The CV of compound IIa (Figure 1) at 100 mVs^{-1} revealed two well-defined cathodic peaks at 0.1 and -0.75 V versus Ag/AgCl electrode. One well defined anodic peak at -0.15 V was observed on the reverse scan suggesting the irreversible nature of the observed electrochemical process in the employed potential range (-2.0 - 2.0 V). On raising the scan rate (>100 mV s^{-1}), the potential of the two cathodic peaks were shifted cathodically, while the anodic peak shifted anodically confirming the irreversible nature of the observed electrochemical processes [24]. The observed cathodic peaks are most likely assigned to the reduction of the carbonyl group via $2\text{H}^{+/2e}$ in two successive one electron / one proton reduction steps [24]. Continuous scan of the CV significantly decreased the peak current height indicating passivity of the surface of the Pt electrode via formation of polymeric oxidation product or fouling of the Pt electrode by the produced reduction products suggesting prior adsorption on the surface of the electrode in the potential range [24].

In DMF- TMA⁺.Cl⁻ the CVs of the compound IVa (Figure 2) at the Pt working electrode showed two reduction peaks at 0.1 -0.15 and -0.65 - -0.8 V coupled with one broad anodic peak in the potential range 0.3-0.4 V at scan rates of 50-1000 mVs^{-1} versus Ag/AgCl electrode. The cathodic peaks are safely assigned to the reduction of the carbonyl group in two successive $\text{H}^{+/e}$ redox steps [18]. The peak –peak potential difference ($\Delta E_p = (E_{p,a} - E_{p,c})$) between the cathodic ($E_{p,c}$) and anodic peaks ($E_{p,a}$) indicated that, the observed redox processes are irreversible. On raising the scan rate both cathodic and anodic peaks are shifted to more negative and positive potential, respectively confirming the irreversible nature of the observed redox process (Bard and Faulkner, 1980). The plot of the the cathodic peak current ($i_{p,c}$) versus the square root of the scan rate was linear indicating that the electrochemical processes is diffusion controlled processes [24]. The plot of $E_{p,c}$ versus log scan rate was found linear at Ag/AgCl. Thus, it can be concluded that, the first reduction processes of the compound precede according to the well known electrode- coupled (EC) chemical reaction mechanism [24].

Retention behavior of bismuth (III) onto reagent IVa immobilized PUFs

In preliminary experiments the use of the reagent IVa immobilized PUFs for the extraction of bismuth (III) from aqueous solution was



examined by batch mode of separation. Reasonable amount of bismuth (III) ions are retained onto the reagent immobilized PUFs from the test aqueous solutions and the amount of bismuth (III) retained on the PUFs depends on the solution pH. Thus, the sorption profile of bismuth (III) at selected concentration (10.0 $\mu\text{g mL}^{-1}$) from the test aqueous solution (50.0 mL) containing excess of KCl, KBr or KI at different pH (pH 2 -8) onto the reagent loaded foams was examined. After shaking the solutions for 2 h, the amount of bismuth (III) remained in the aqueous solution was determined. The amount of bismuth (III) retained, the extraction percentage, %E and the distribution ratio, D

was then calculated as reported earlier [19-21]. Maximum retention of bismuth (III) by the immobilized reagent PUFs was achieved from the aqueous media at pH 2-3 containing iodide ions and the sequence of the uptake followed the order: iodide>bromide>chloride. The uptake of bismuth (III) from the aqueous iodide media decreases on increasing the solution pH.

The observed decrease on the bismuth (III) retention at pH>3.5 is most likely attributed to the instability of bismuth-iodide or the ternary complex involving $[\text{BiI}_4]^{-}\text{IVa}^{+}$ due to the hydrolysis of the species formed between $[\text{BiI}_4]^{-}$ and the reagent immobilized polyurethane foams. Similar trends were also reported earlier [19-21]. Thus, a "weak base anion ion exchanger" and a "solvent extraction" mechanism of the $[\text{BiI}_4]^{-}(\text{aq})$ may be proposed for the uptake onto the protonated ether ($-\text{CH}_2-\text{HO}^+-\text{CH}_2-$) or urethane ($-\text{NH}^2\text{COO}-$) linkages of the immobilized PUFs.

The effect of contact time and shaking time on the retention of bismuth by the treated AMP-PUFs of bismuth (III) from the aqueous solution containing high excess of KI (5-7% w/v) by AMP-loaded foam was carried out at pH 2.0. The bismuth (II) uptake was fast and reached maximum within ~ 10-15 min contact time. The half-life time ($t_{1/2}$) of the equilibrium sorption of bismuth (III) as calculated from the plot of $-\log(C_b - C_a)/C_b$ versus time onto the reagent immobilized PUFs from the aqueous media to reach 50% saturation of the sorption capacity was in the range 1-1.5 min (Figure 3). The uptake of bismuth (III) ions was fast within the first 10 min and increased up to a constant value in less than 60 min shaking time. Thus, a shaking time of 60 min was adopted in subsequent experiments.

Conclusion

The redox behavior of the tested compounds suggest the possible application of the compounds as chelating agent for the determination of ultra trace concentration of heavy metal ions employing differential pulse - adsorptive stripping voltammetry. Moreover, immobilization of one of the prepared compounds on polyurethane foam solid sorbent as trapping agent for minimization and/or separation of bismuth (III) from industrial wastewater was achieved. Work is still continuing for application of the compound in cathodic stripping voltammetric procedures for trace metal analysis in different matrices.

Acknowledgement

The authors would like to thank the Deanship of Scientific Research, King Abdul Aziz University, Saudi Arabia for the financial support under the grant number 428/173 and the Department of Chemistry for the facilities provided.

References

- Funk RL, Fitzgerald JF, Olmstead TA, Para KS, Wos JS (1993) J Am Soc 115: 8849.
- Zheng H, Swager TM (1994) Octahedral Metallomesogens: Liquid Crystallinity in Low Aspect Ratio Materials. J Am Chem Soc 116: 761-762.
- Sievers RE, Turnispeed SB, Huang L, Laglante AF (1993) Volatile barium β -diketonates for use as MOCVD precursors. Coord Chem Rev 128: 285-291.
- Knoevenagel E, Arnot R (1904) Condensationen von Salicylaldehyd mit Cyanessigester, Benzoylessigester und Acetylaceton. Chem Ber 37: 4499.
- Kailash D (1991) Trans Met Chem16: 73.
- Abdul Samath S, Raman M, Raman N, Jeayasubramanian K, Ramalingam S K (1992) Cobalt(II), nickel(II), copper(II) and zinc(II) complexes of conjugated 3-(benzylidene/salicylidene)- β -diketonates (having no enolisable γ -carbon proton) and their reactions. Trans Met Chem 17: 13-15.
- Wang QL, Yudao M, Bojun Z (1997) Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry. Synth Commun 27: 4107- 4110.

8. Veeraraj A, Sami P, Rahman N (2000) Copper (II) complex of 3-cinnamalideneacetylacetone: Synthesis and Characterization. *Proc Indian Acad Sci (Chem Sci)* 112: 515 -521.
9. Abdel-Rahman RM, Seada M, Fawzy MM (1991) *Pak J Sci Ind Res* 34: 465.
10. Ramadan AAT, Abdel- Rahman RM, El-Behairy MA, Al Ismail MM (1993) The thermodynamics of complexation of transition and lanthanide ions by 3-(α -carboxymethylaminobenzylidenehydrazino)-5,6-diphenyl-1,2,4 triazine (HipHt) Mahmoud. *Thermochimica Acta* 222: 291- 303.
11. Abdel-Rahman RM (1998) *Indian J Chem* 27: 548.
12. Arrieta A, Dietze F, Mann G, Beyer L, Hartung H (1988) *J Prakt Chem* 330: 111.
13. Tuchinda PT (1994) *J Indian Chem Soc* 71: 509.
14. Venugopalan P, Krishnankutty K (1998) Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry. *Synth React Inorg Metal- Org Chem* 28: 1313-1325.
15. Krishnankutty K, Venugopalan P (2001) Metal chelates of 6-aryl-5-hexene-2,4-diones. *J Indian Chem Soc* 78: 472 -473.
16. Cerchiaro G, Ferreira AM, Teixeira AB, Magalhaes HM, Cunha AC, et al. (2006) Synthesis and crystal structure of 2,4-dihydro-4-[(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)imino]-5-methyl-2-phenyl-3H-pyrazol-3-one and its copper(II) complex. *Polyhedron* 25: 2055-2064.
17. Krishnankutty K, Ummathur MB (2006) *J Indian Chem Soc* 83: 639-663.
18. Bashammakh AS, Al-Shareef FM, El-Shahawi MS (2009) Development of an Analytical Method for Trace Gold in Aqueous Solution Using Polyurethane Foam Sorbents: Kinetic and Thermodynamic Characteristic of Gold (III) Sorption. *Anal Sci (Japan)* 25: 413-418.
19. El-Shahawi MS, Abou-Mesalam MM, El-Naggar IM (2003) Radioanal Use of open-cell resilient polyurethane foam loaded with crown ether for the preconcentration of uranium from aqueous solutions. *J Nucl Chem* 258: 619.
20. El-Shahawi MS, Othman MA, Abdel-Fadeel MA (2005) Kinetics, thermodynamic and chromatographic behaviour of the uranyl ions sorption from aqueous thiocyanate media onto polyurethane foams. *Anal Chim Acta* 546: 221-228.
21. El-Shahawi MS, SSM Hassan MA (2008) El-Sonbati *Microchem Retention profile and subsequent chemical speciation of chromium (III) and (VI) in industrial wastewater samples employing some onium cations loaded polyurethane foams. Microchemical J* 89: 13-19.
22. Farag AB, Soliman MH, El-Shahawi MS (2007) *Anal Chim Acta* 601: 218-221.
23. Zaki MT, Abdel-Rahman RM, El-Syed AY (1995) Use of arylidenerhodanines for the determination of Cu(II), Hg(II) and CN⁻. *Anal Chim Acta* 307: 127-138.
24. Bard AJ, Faulkner LR (1980) *Electrochemical Methods, Fundamentals and Applications*. Wiley, New York, P. 218.