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Synthesis of Polyfunctional Organic Systems Containing 1- Acyl / Aroyl - anilido-butadienes and their uses as Photochemical Probes and Chelating Agents for Removal of Bismuth (III) from Industrial Wastewater

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Abstract

The present article reports the synthesis of a series of some new 1-acyl/ benzoyl -1-anilido-4-methyl /aryl-1, 3-butadiene derivatives (II - IV) by warming primary heteroamines and/ or sulfa drugs with pre heated ethyl acetoacetate and / or ethyl benzoylacetate in dry conditions followed by condensation with unsaturated aromatic aldehydes in boiling ethanol-piperidine. The chemical structures of the compounds were characterized via their elemental analysis and spectroscopic measurements (UV Vis., IR, ^{1}HNMR). Some of the compounds (IIId, e, f, IV d, e,f) were tested as antimicrobial and photochemical probe agents. Compound IVa was physically loaded onto polyurethane solid sorbent and successfully used for the removal and / or pre concentration of bismuth (III) from industrial wastewater. The voltammetric behavior of the two compounds IIa and IVa in N, N-dimethylformamide was investigated.

Keywords: Synthesis; 1, 3-butadiene derivatives; Photochemical probes; Chelating agent; Bismuth (III); Wastewater; Voltammetry

Introduction

Polyfunctionalally substituted oxo anilides e.g. azoloazines have received considerable interest in recent years (Hussein et al., 2009). Such class of compounds has diverse physiological activities e.g. acting as central nervous systems depressants and calcium sensitizing agents and possess hypnotic, diuretic, antihistaminic, anti inflammatory, antimicrobial and hypoglycecemic activities (Fathalla et al., 2001).The synthesis and spectroscopic characterization of β-diketones as potential ligands have been reported by Funk et al., 1993; Zheng and Swager, 1994. In this class of compounds, complex formation is conceived by replacement of the enolic proton by chelation with metal ions in a bidentate fashion (Sievers et al., 1993; Knoevenagel and Arnot, 1904).

The β- diketone 3- salicylidene-2, 4- pentanediones and related compounds have been used successfully as proper chelating agents for a series of metal ions (Mishra et al., 1991; Wang et al., 1997). Knoevenagel condensates of substituted benzylidenes with active methylene compounds have been performed efficiently using ultra stable Zeolite as heterogeneous catalyst (Veeraraj et al., 2000). The chelation behavior of a series of dicarbonyl towards some metal ions has been reported (Krishnankutty and Venugopalan, 2001). Metal chelates of β- diones have shown interesting properties in particular in industrial applications (Krishnankutty and Venugopalan, 2001; Cerchiaro et al., 2006; Krishnankutty and Ummathur, 2006). Abdel-Rahman et al., 1991; Ramadan et al., 1993; Abdel-Rahman, 1988).

A series of benzoyl -acetanildes and their physico organic properties have been reported by (Abdel-Rahman, 1988; Abdel-Rahman et al., 1991). The starting material prepared has been used for building a series of novel bio- active pyrazoline derivatives. The thermodynamic characteristics and spectroscopic characterization of a series of hydrazono – 1,3- bi carbonyl derivatives and their lanthanide complexes have been investigated (Abdel-Rahman et al., 1991; Ramadan et al., 1993).The dimerized species of 2- diazo-3-methyl-1- phenyl-5- pyrazolone have produced 4- (5-hydoxy-4-pyrazolxlimino-2-pyrazolin-5- one.

Recent literature survey has indicated that, no work on the Knoevenagel condensate β- ketoanilide and its metal chelates. Therefore, in continuation to our previous work (Bashammakh et al., 2009; Abou-Mesalam et al., 2003; El-Shahawi et al., 2005; El-Shahawi et al., 2008; Farag et al., 2007; Zaki et al.1995), the present study is focused on the synthesis and characterization of a series of some β-diketone derivatives bearing anilido moieties and their unsaturated β- diketone derivatives. In view of their properties, some of the compounds were tested as antimicrobial and photochemical agents. Moreover, one of the prepared compounds for the pre-concentration/ separation of bismuth (III) from aqueous as a highly toxic metal ions the industrial waste water. The cyclic voltammetry of two selected compounds were also investigated.

Experimental

Apparatus & 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. A Perkin-Elmer (Analyst TM 800, USA) atomic absorption spectrometer (AAS) was used for measuring the concentration of bismuth (III) ions before and after extraction at the optimum operational parameters of the instrument. A Perkins Elmer model RXI-FT-IR system 55529 was used for recording the IR spectra of the prepared compounds. A Brucker advance

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DPX 400 MHz model using TMS as an internal standard was used for recording the ^{1}HNMR spectra of the compounds on deuterated DMSO. A GC-MS-QP 1000-Ex model was used for recording the mass spectra of the compounds. 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. Digital pH-meter (model MP220, Metter Toledo) was used for pH measurements. Melting points were determined with an electro thermal Bibbly Stuart Scientific Melting Point SMPI (US). Molecular weights and elemental analysis of the compounds were preformed on Micro analytical center, Cairo University, Egypt. Microanalysis of nitrogen and sulfur (%) was performed in Microanalytical Center, Ain-Shams University, Cairo, Egypt.

Reagents & materials

Low density polyethylene (LDPE) bottles, Nalgene were carefully cleaned first with hot detergent, soaked in 50% HCl (Analar), HNO_3 (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 2-10 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 (0.20mol L^{-1}). A stock BDH stock solution of bismuth (1000 μg mL^{-1}) in dilute nitric acid was used. A series of standard bismuth (III) solutions in the range 1-100 μg mL^{-1}) was then prepared in doubly distilled water in the presence of few drops of nitric acid (5% m/v). Stock solutions (1x 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.

Organic preparation

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).

Preparation 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 PUFs 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 (Abou-Mesalam et al., 2003; El-Shahawi and El-Sonbati, 2005; El-Shahawi et al., 2008). 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±0.01g) 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 2-10). 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 (C_o) and after (C_a) shaking with the foam cubes.

Results and Discussion

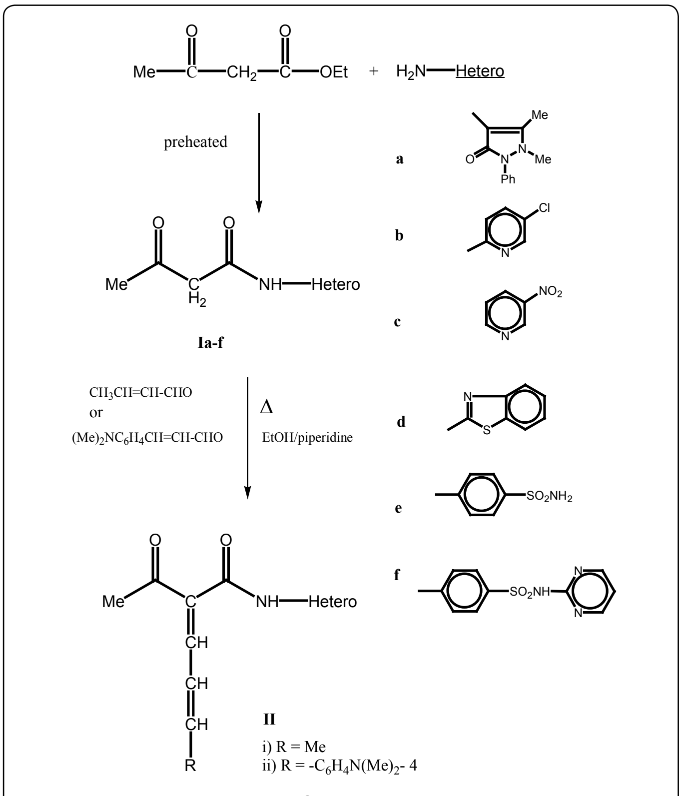
Spectroscopic characterization

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

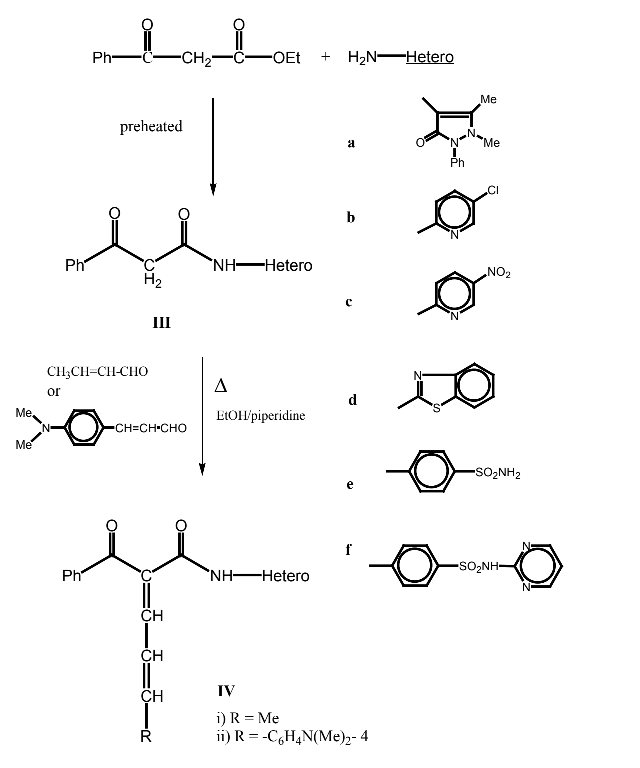
Compd No.	M.P. (°C)	Yield (%)	Solvent	M. Formula	M. Weight		Nitrogen, %*		Sulfur. %*	
					Found	Calcd	Found	Calcd	Found	Calcd
Ia	130	80	Pet. ether 60-80	$C_{15}H_{17}N_3O_3$	285	287	13.10	14.63	-	-
Ib	165	70	Pet. ether 60-80	$C_9H_9N_2ClO_2$	210	212	13.42	13.20	-	-
Ic	158	75	Pet. ether 60-80	$C_9H_9N_3O_4$	221	223	17.73	18.81		
Id	225	75	Pet. ether 60-80	$C_{11}H_{10}N_2SO_2$	231	234	11.52	11.96	13.43	13.40
Ie	135	80	Pet. ether 60-80	$C_{10}H_{12}N_2SO_4$	254	256	9.99	10.93	12.35	12.5
If	210	85	Pet. ether 60-80	$C_{14}H_{14}N_4SO_4$	333	334	16.64	16.76	9.46	9.58
IIa	150	72	THF	$C_{20}H_{20}N_4O_4$	377	380	14.61	14.73	-	-
IIb	170	75	THF	$C_{15}H_{14}N_2SO_2$	284	286	8.85	9.79	11.04	11.18
IIIa	140	73	Pet. Ether 100-140	$C_{20}H_{19}N_3O_3$	345	349	11.21	12.03		
IIIb	170	78	Pet. Ether 100-140	$C_{14}H_{11}N_2ClO_2$	273	275	9.51	1018		
IIIc	162	80	Pet. Ether 100-140	$C_{14}H_{11}N_3O_4$	283	285	13.7	14.73		
IIId	300	90	Pet. Ether 100-140	$C_{16}H_{12}N_2SO_2$	296	296	8.55	9.45	10.57	10.81
IIIe	240	85	Pet. Ether 100-140	$C_{15}H_{14}N_2SO_4$	314	318	7.90	8.80	9.83	10.06
IIIf	335	82	Pet. Ether 100-140	$C_{19}H_{16}N_4O_4$	396	396	12.93	14.14	-	-
IVa	125	70	Diethyl ether	$C_{25}H_{22}N_4O_4$	441	442	12.2	12.66	-	-
IVb	280	72	Diethyl ether	$C_{20}H_{16}N_2SO_2$	346	348	7.1	8.04	8.88	9.19
IVc	140	60	Diethyl ether	$C_{27}H_{23}N_3SO_2$	451	453	8.5	9.27	6.9	7.06

*Analytical data of **C** and **H** for the compounds are within the range ± 0.4-0.7% of the theoretical values.

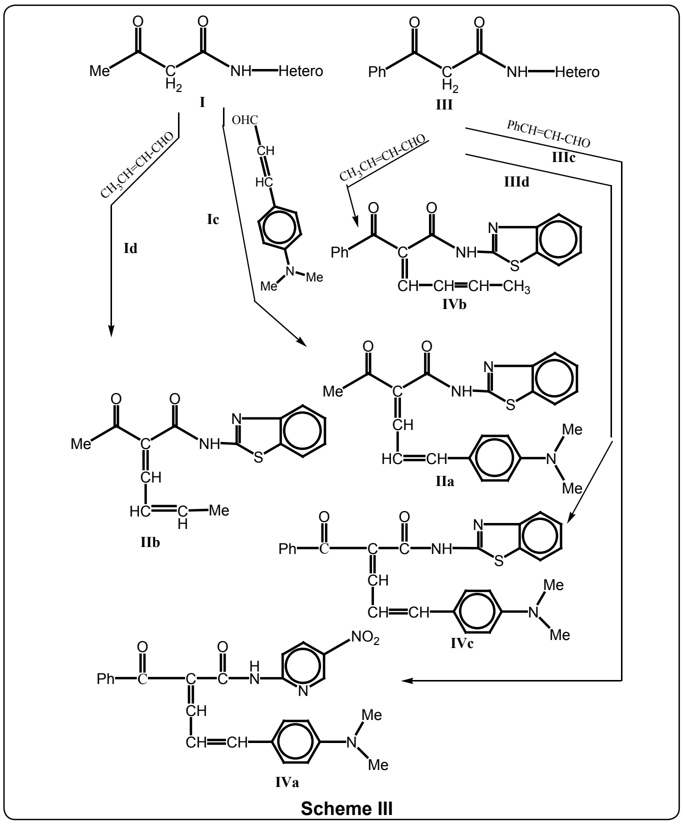
Table 1: Physical properties of prepared compounds I-IVc.



Scheme I



Scheme II



Scheme III

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/bezoyl 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. The compounds prepared are summarized in schemes 1-III. Both carbonyl compounds I-IV having a second carbonyl at β -position, are termed as β 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 (Mishra et al., 1991) 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 ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions) 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 (Sawyer et al., 1984).

IR spectra of compounds I and III show no characteristic C=O absorption band at ν 1725-1710 cm^{-1} which is present in the spectrum of acetylacetone ~ 1680 cm^{-1} while that of II and IV recorded of strong absorption bands at ν 1650 cm^{-1} of true C=O group. Also, intarmolecular 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.

^{1}HMNR spectra of compounds I and III showed a one proton signal at $\delta\sim15$ ppm confirming the presence of strong intramolecular hydrogen bonded enol proton, in addition, a signal appeared at δ 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, ^{1}HMNR 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. The tautomeric forms of compounds I and III were confirmed via ^{1}HMNR where, one resonated singlet for proton linked to sp^3-carbon at δ 4.66 ppm was noticed. The structures of the compounds Id and IIId were deduced from ^{13}C NMR. The spectrum of compound Id showed 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 IIId revealed 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). Based on ^{1}H and ^{13}C NMR data, the acy/benzoyl anilide derivatives are mainly present in enolic structure with intra molecular hydrogen bonding in solution state. The acyl/benzoyl anilides existed predominantly in the cis- form via some type of interaction.

Mass spectra of compounds I-IV confirmed the degree of stability as indicated from the equilibrium between ketonic and enolic forms. Fragmentation also revealed the loss of Me-CO and Ar-CO from their chemical 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 (Mishra et al., 1991).

Applications of the prepared compounds

Biocidal activity: Some of the synthesized compounds were tested *in-vitro* against microorganisms such as bacteria *Escherichia. Coli* and the fungi *Aspergillums fumigates* in DMF using the agar diffusion disk method (Barry et al., 1981; Winker et al., 1962). The results are compared with pipercillin and mycostatine as standard antibiotic. The antimicrobial potentialities of the tested compounds were evaluated by placing pre sterilized filter paper disks (11 mm diameter) impregnated with 50 mg/disk using DMSO as solvent which revealed no zone (IZ) after 5 days incubation at 28°C for fungi (Table 2). Photochemical probe effects of these compounds were determined before and after using UV light at 366 nm as a second test (Table 2). The compounds IIIe,d,f and IVe,d,f showed a highly biocidal effect and only compounds IIIe,d,f were found characterized by photo chemical probe action lower than other prepared compounds. This behavior is most likely attributed to the rich oxygen atoms in their structures with multi excitation states.

Pre concentration and / or separation of bismuth (III) onto reagent IVa immobilized PUFs

In preliminary experiments the use of the reagent IVa immobilized PUFs for the pre concentration 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. The amount of bismuth (III) retained on the reagent treated PUFs depends on the solution pH. Thus, the sorption profile of bismuth (III) (10.0 μg mL^{-1}) from aqueous solutions (50.0 mL) containing excess of KCl, KBr or KI at different pH (pH 2 -10) 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 by. The amount of bismuth (III) retained, the extraction percentage, %E and the distribution ratio, D was then calculated as reported earlier (Abou-Mesalam et al., 2003; El-Shahawi et al., 2005; El-Shahawi et al., 2008). Maximum retention of bismuth (III) by the immobilized reagent PUFs was achieved from the aqueous media of pH 2-3 containing excess iodide ions and the sequence of bismuth (III) uptake followed the order:

iodide> bromide > chloride.

Compound 50 mg/mL	Before UV irradiation		After UV irradiation at 366 nm	
	Bacteria Escherichia coli	Fungi Asperigillus fumigates	Bacteria Escherichia coli	Fungi Asperigillus fumigates
IIId	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 mm; moderate (15 – < 20 mm) and weak < 15 mm.

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

On the other hand, the retention 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 $[BiI_4]^-$. IVa $^+$] due to the hydrolysis of the species formed between $[BiI_4]^-$ and the reagent immobilized polyurethane foams. Similar trends were also reported earlier (Abou-Mesalam et al., 2003; El-Shahawi and El-Sonbati, 2005; El-Shahawi et al., 2008). Thus, a "weak base anion ion exchanger" and a "solvent extraction" mechanism of the $[BiI_4]^-_{(aq)}$ may be proposed for the uptake onto the protonated ether ($–CH_2–HO^+–CH_2–$) or urethane ($–NH^+{}_2COO-$) 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 1). 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.

The analytical utility of the reagent IVa treated PUFs solid sorbent was successful assessed using the reagent IVa immobilized PUFs in packed column for complete retention of different concentrations (100 mL, 5-1000 μgL^{-1}) of bismuth (III) in de ionized water. The sample solutions were percolated through the PUFs packed column

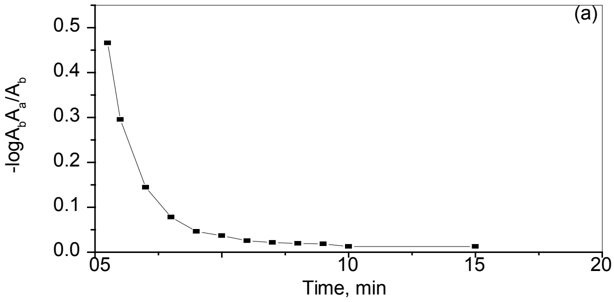


Figure 1: Rate of sorption of bismuth (III) ontothe reagent AMP-loaded foams at 35°C onto the reagent AMP immobilized foams.

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Bismuth (III) species		Recovery, %*
Added, µg/mL	Found, µg/L	
1.0	0,98	96.0± 1.8
5.0	4.7	94.0± 2.7

*Average ± relative standard deviation

Table 3: Retention and recovery of bismuth (III) in wastewater samples by the reagent IVa treated PUFs packed column.

at flow rate of 10 ml min^{-1}. Quantitative retention of bismuth (III) was achieved onto PUFs packed column as noticed from the analysis of bismuth in the effluent solutions by FAAS.

The removal of bismuth (III) from industrial wastewater was also carried out following the same procedures. The water samples of industrial wastewater (0.1 L) of electroplating industry after acidified with phosphoric acid was spiked with various concentrations (1 and 5 µgmL^{-1}) of bismuth (III), acidified with phosphoric acid and filtered through a 0.45 µm cellulose membrane filter. The test water samples were percolated through the reagent packed column at 5 mL min^{-1} flow rate. The analysis of bismuth in the effluent solution by FAAS revealed complete retention of cadmium from the test solution. The results are summarized in Table 3. Bismuth was quantitatively recovered with acidified solution of nitric acid (10 mL, 3.0 M) and analyzed by FAAS. A satisfactory recovery percentage of total cadmium was achieved in the range 94 – 96 .0±2.7.

Voltammetric study

The cyclic voltammograms (CVs) of the 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 Figure 2 and Figure 3. The CV of compound IIa (Figure 2) 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 (Bashammakh et al., 2009; Bard and Fulkner, 1980). The observed cathodic peaks are most likely assigned to the reduction of the carbonyl group via 2H$^+$/2e in two successive one electron / one proton reduction steps (Bard and Fulkner, 1980). 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 (Bard and Fulkner, 1980).

In DMF- TMA$^+$.Cl$^-$ the CVs of the compound IVa (Figure 3) 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 H$^+$/e redox steps (Bashammakh et al., 2009). 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 Fulkner, 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 (Bard and Fulkner, 1980). 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 (Bard and Fulkner, 1980). The overall results suggest the possible use of the two compounds as complexing agent in cathodic stripping voltammetry for determination of bismuth (III) ions (II) in water.

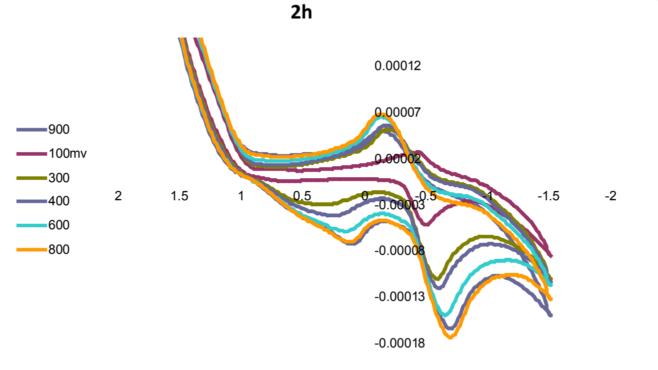

Figure 2: Cyclic voltammograms of the compound 1-acyl-1-anilido-4- methyl-1, 3- butadiene, IId in DMF-TMA$^+$.Cl$^-$ at Pt working electrode *vs.* Ag/AgCl electrode at various scan rates.

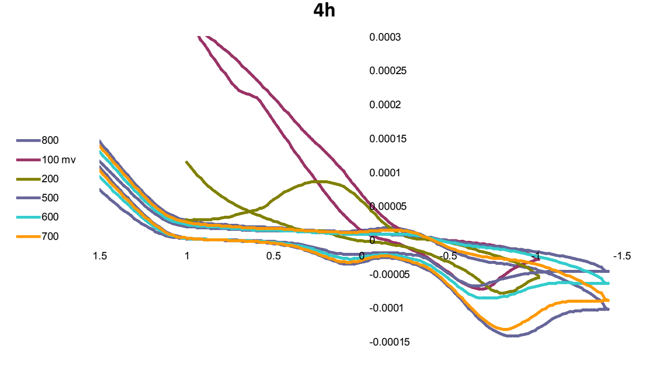

Figure 3: Cyclic voltammograms of 1-benzoyl-1-anilido-4- methyl-1, 3-butadiene, IVd in DMF-TMA$^+$.Cl$^-$ at Pt working electrode *vs.* Ag/AgCl electrode at various scan rates.

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.

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References

1. Abdel- Rahman RM, Seada M, Fawzy MM (1991) Synthesis and antimicrobial activity of some new 3,5- disubstituted pyrazolines containing 1,2,4 – triazine moiety. Pak J Sci Ind Res 34: 465-469.
2. Abdel-Rahman RM (1988) Reactions of 3 – hydrazine-5,6 – diphenyl-1,2,4-triazine withunsymmetrical 1,3 – bicarbonyl compounds: synthesis of some new 3-(3,3–disubstituted pyrazinol -1-yl-5,6- diphenyl= 1,2,4- triazines and their antimicrobial activities. Indian J Chem 27 B: 548 -553.
3. Abou-Mesalam MM, El-Naggar IM, Abdel-Hai MS, El-Shahawi MS (2003) Use of open-cell resilient polyurethane foam loaded with crown ether for the preconcentration of uranium from aqueous solutions. J Radioanal Nucl Chem 258: 619 -625.
4. Bard AJ, Faulkner LR (1980) Electrochemical Methods, Fundamentals and Applications. Wiley New York pp 218-235.
5. Bashammakh AS, Bahaffi SO, Al-Shareef FM, El-Shahawi MS (2009) Development of an Analytical Method for Trace Gold in Aqueous Solution using Polyurethane Form Sorbents: Kinetic and Thermodynamic Characteristic of Gold (III) Sorption. Anal Sci (Japan) 25: 413-418.
6. Barry AL, Thomsbery C (1981) Susceptibility Testing Diffusion Testes Procedures in Manual of Clinical Microbiology. American Society for Microbiology, Washington, P. 561.
7. Cerchiaro G, Ferreira AMD, Teixeira AB, Magalhães HM,Cunha AC· Ferreira VF, 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.
8. Claeson P, Tuchinda P, Reutrakul V (1994) Natural Occurring 1,7-diarylheptanoids. J Indian Chem Soc 71: 509-521.
9. El-Shahawi MS, El-Sonbati MA (2005) Retention profile, kinetics and sequential determination of selenium (IV) and (VI) employing 4,4’-dichlorodithizone immobilized-polyurethane foams. Talanta 67: 806-815.
10. El-Shahawi MS, Hassan SSM, Othman AM, El-Sonbati MA (2008) 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.
11. El-Shahawi MS, Othman MA, Abdel-Fadeel MA (2005) Kinetics, thermodynamic and chromotographic behavior of the uranyl ions sorption from aqueous thiocyanate media onto polyurethane foams. Anal Chim Acta 546: 221-228.
12. Farag AB, Soliman MH, Abdel-Rasoul OS, El-Shahawi MS (2007) Sorption characteristics and chromatographic separation of gold (I& III) from silver and base Metal ions using polyurethane foams. Anal Chim Acta 601: 218-229.
13. Fathalla WM, Cajan M, Marek J, Pazdera P (2001) One-Pot Quinazolin-4-ylidenethiourea Synthesis via *N*-(2-Cyanophenyl)benzimidoyl isothiocyanate. Molecules 6: 574-587.
14. Funk RL, Fitzgerald JF, Olmstead TA, Para KS, Wos JA (1993) Titanium-mediated cyclizations of beta-keto esters with acetals: a convenient route to 2-carbalkoxycyclo- alkenones. J Am Chem Soc115: 8849-8850.
15. Hussein AHM, El-Gaby MS, Abu-Shanab, Abdel-Raheim MAM (2009) β-Oxo anilides in heterocyclic synthesis: Synthesis of tri- and tetracyclic containing a bridgehead nitrogen atom Org. Commun 2: 66-71.
16. Knoevenagel E, Arnot A (1904) Condensation of salicylaldehyde and cyanoester, benzoylester and acetylacetone. Ber 37: 4496-4499.
17. Krishnankutty K, Ummathur MB (2006) Metal complexes of unsaturated diketo anilides. J Indian Chem Soc 83: 639,663,88.
18. Krishnankutty K, Venugopalan P (1998) Metal chelates of curcuminoids. Synth. React. Inorg. Metal- Org. Chem 28: 1313-1325.
19. Krishnankutty K, Venugopalan P (2001) Metal chelates of 6-aryl-5-hexene-2,4-diones. J Indian Chem Soc 78: 472 -473.
20. Mishra PK, Chakravortty V, Dash KC (1991) Schiff base complexes of zirconium (IV) derived from Zr (acac) 4. Trans Met Chem 16: 73-75.
21. Ramadan AAT, Abdel- Rahman RM, El-Behairy MA, Ismail AI, Mahmoud MM (1993) Thermodynamics of complexation of transition and lanthanide ions by 3 – (α- carboxymethylaminebenzylidene hydrazino)-5,6-diphenyl-1,2,4- triazine. Thermochim Acta 222: 291-303.
22. Sawyer DT, Heinemann WR, Beebe JM, Reilley CN (1984) Chemistry Experiments for Instrumental Methods. John Wiley & Sons PP 215-221.
23. Sievers RE, Turnispeed SB, Huang L, Laglante AF (1993) Volatile barium β diketonates for use as MOCVD precursors. Coord Chem Rev 128: 285-291.
24. Veeraraj A, Sami P, Rahman N (2000) Copper (II) complex of cinnamalideneacetylacetone: Synthesis and Characterization. Proc Indian Acad Sci112: 515 -521.
25. Wang QL, Yuado M, Bojun Z (1997) Knoevenagel condensation by USY Zeolite. Synth. Commun 27: 4107-4110.
26. Winker CA, Risley EA, Nuss GW (1962) Procedure Society Experimental. Biology Medicinal 111: p544.
27. 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.
28. Zheng H, Swager TM (1994) Octahedral Metallomesogens: Liquid Crystallinity in Low Aspect Ratio Materials. J Am Chem Soc 116:761-2.