PREPARATION AND EVALUATION OF SOME SURFACE ACTIVE AGENTS AND THEIR APPLICATION AS CHELATES FOR SOME HEAVY METALS.

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ABSTRACT

A novel series of chelating agents has been synthesized by the reaction of ethylenediaminetetraacetic acid, trimercaptotriazine and polyethylene glycol with different number of moles. The unique structural features of these surfactants have been confirmed by FTIR spectra, elemental analysis and H^1NMR spectrum. These surfactants exhibit excellent properties in chelating heavy metal such as copper, lead and mercury. They show good surfactant properties, including surface tension, effectiveness, efficiency and emulsifying power. Critical micelle concentration, maximum surface excess and minimum surface area have been studied. Free energy of micellization and adsorption have been calculated.

INTRODUCTION

Toxic heavy metal in air, soil and water are global problems that are growing threat to the environment. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, mining, and cholor-alkali industries **[Alloway, (1995) and Henke, et al. (1993)]**. Although there are many technologies for heavy metal remediation, the use of chemical chelates has only recently come under systematic investigation **[Evanko (1997)]**.

Mercury, lead and copper are three heavy metals that are abundant in the ecosystem of the earth and available largely due to anthropogenic sources. It has been estimated that mercury emissions globally exceed 3000 tons annually **[Schroeder, (1998)]**. The element can be found in air, sediments, soils, sea water and fresh water. Effects

of the high levels of mercury in blood and hair can be correlated with sensory disturbances (paresthesia, hypaesthesia), constriction of the visual field, hearing impairment, and neurological disturbance [**Sittig, (1995)**]. Lead is toxic with various detrimental biological effects including inhibition of the synthesis of hemoglobin [**Manahan, (1994)**], disfunction in the kidneys, reproductive system, liver, and the central and peripheral nervous systems [**Sittig, (1985) and Derelanko, (1995)**]. Copper also can cause accute effects such as GL disturbances, damage to the liver and renal systems and anemia.

Accordingly, it has been the focus of our research to synthesize a series of chelate surfactants for heavy metals, which result soluble metal ligand complexes. These chelate surfactants appear to have high affinity for metals. These surfactants were synthesized by the reaction of ethylenediaminetetra acetic acid, (EDTA), trimercaptotriazine and poly ethyleneglycol (600) with different number of moles (1,2 or 3).

EXPERIMENTAL PROCEDURE

Materials:
All the chemicals used throughout this investigation are submitted from international companies. All of them were in analytical grade as shown in Table 1.

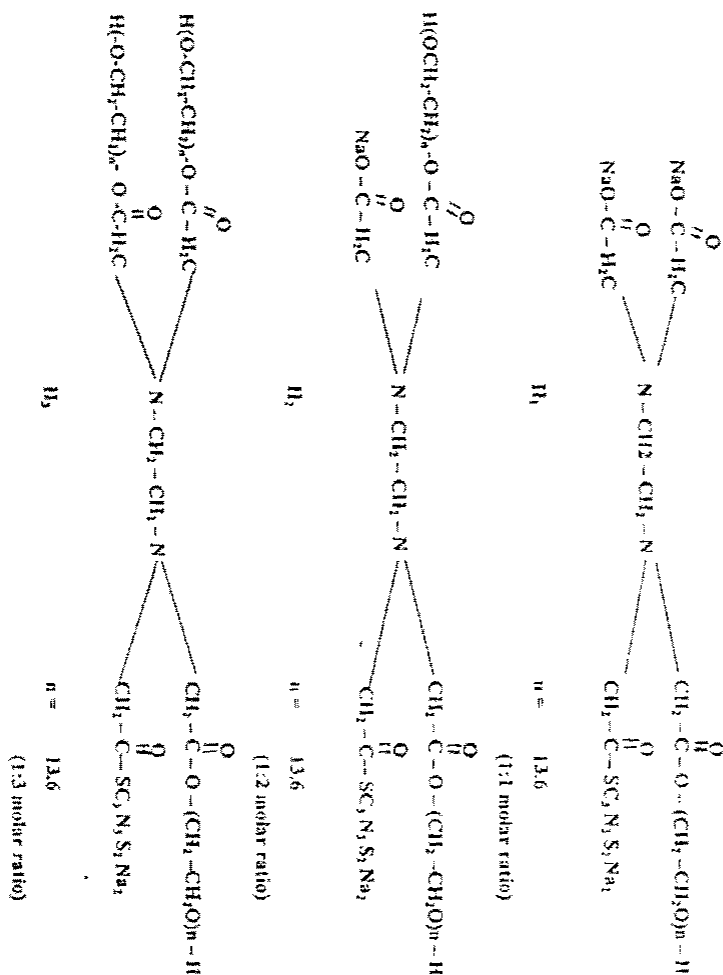**Table (1):** Chemical used throughout the investigation.

Material	Molecular weight	m.p, °C	Source
EDTA	292	52	Hungary Co
Trimercaptotriazine	177.2	-	Aldrich
Polyetheleneglycol (PEG)*			
E.O.13.6	600	22	Aldrich

* where in, E.o = number of ethylene oxide units, which are coming from the corresponding M.Wt of (PEG).

Synthetic procedure
The chelate surfactants were prepared by stoichiometric amounts of reacting EDTA with trimercaptotriazine in benzene in presence of hydrochloric acid as a catalyst (36.5%, 2mL) until the desired amount of water (0.1 mole, 1.8 ml) was removed. The removal of excess solvent was performed in rotary evaporator under reduced pressure. The

compound obtained reacts with molecular weight of PEG (600) by different molar ratio (1:1, 1:2 or 1:3) followed by neutralization with NaOH to get three of chelating surfactants. The purification of products was carried out by ethanol. To form semisolid compounds, these ligands were designated by (II_1, II_2 and II_3).

$$NaO-\overset{O}{\underset{\parallel}{C}}-H_2C \diagdown \diagup N-CH_2-CH_2-N \diagup \diagdown CH_2-\overset{O}{\underset{\parallel}{C}}-O-(CH_2-CH_2O)n-H$$

$$NaO-\overset{O}{\underset{\parallel}{C}}-H_2C \qquad\qquad CH_2-\overset{O}{\underset{\parallel}{C}}-SC, N_3 S_2 Na_2$$

$$II_1 \qquad n = 13.6 \qquad (1:1 \text{ molar ratio})$$

$$H(OCH_2-CH_2)_n-O-\overset{O}{\underset{\parallel}{C}}-H_2C \diagdown \diagup N-CH_2-CH_2-N \diagup \diagdown CH_2-\overset{O}{\underset{\parallel}{C}}-O-(CH_2-CH_2O)n-H$$

$$NaO-\overset{O}{\underset{\parallel}{C}}-H_2C \qquad\qquad CH_2-\overset{O}{\underset{\parallel}{C}}-SC, N_3 S_2 Na_2$$

$$II_2 \qquad n = 13.6 \qquad (1:2 \text{ molar ratio})$$

$$H(O-CH_2-CH_2)_n-O-\overset{O}{\underset{\parallel}{C}}-H_2C \diagdown$$
$$H(O-CH_2-CH_2)_n-O-\overset{O}{\underset{\parallel}{C}}-H_2C \diagup N-CH_2-CH_2-N \diagup \diagdown CH_2-\overset{O}{\underset{\parallel}{C}}-O-(CH_2-CH_2O)n-H$$
$$CH_2-\overset{O}{\underset{\parallel}{C}}-SC, N_3 S_2 Na_2$$

$$II_3 \qquad n = 13.6 \qquad (1:3 \text{ molar ratio})$$

METHODS OF ANALYSIS AND INSTRUMENTS

FTIR measurements

Infrared spectra for prepared surfactants was measured using Avatar 230 FTIR spectrophotometer to measure intensity of absorption bands for the prepared surfactants. The measurements were carried out at Egyptian Petroleum Research Institute.

Elemental Analysis Measurements

The elemental analysis for the obtained surfactants were carried out using Elemental Analyzer Model Varioelementar. The measurements were carried out at National Research Center.

Proton Nuclear Magnetic Resonance Measurements

H^1NMR analyses were performed on a Varian-Gemini-200 instrument and the samples were run in deuterated chloroform ($CDCl_3$, Cambridge Isotope Laboratories)

Atomic Absorption Spectrometer (AAS) measurements

Copper, lead and mercury analyses were performed with ASS (Flame absorption) perkinelmer. The detection limits for these analysis are 0.02 mg/L for Cu, 0.007mg/L for lead and 0.0068mg/L for Hg.

Evaluation Methods of Surface Active Properties
Surface and interfacial tension measurements

Surface and interfacial tension measurements of the prepared surfactants were made at room temperature (25°C) with Du Nouy tensiometer (Kruss type 8451) using distilled water solution of 0.1% weight concentration [**Findlay, (1963)**].

The surface tension of the used distilled water was 73 mN/m and the interfacial tension between paraffin oil and distilled water was 56.2 mN/m. Surfactant solution were aged for 2h before any measurements were made. Three readings were made on each sample to determine any change with time and to obtain an average value [**Hampson and Cornell (1996)**].

Emulsifying power

In a measuring cylinder, surfactant solution (0.1g/L, 10ml) and paraffin oil (10ml) were mixed. After vigorous shaking (20 times), the

tube was allowed to stand till any separation of the two phases appeared. Emulsifying power or emulsifying time (in sec) was determined according to the method described elsewhere [Takeshita & Maeda (1980) Takeshita & Maeda (1982)].

Efficiency (PC$_{20}$)

PC$_{20}$ value measures the efficiency of adsorption of the surfactant at the interface [Bhattacharyya, et al., (1994)] and it is measured by negative logarithm of the surfactant molar concentration (mol/L) required to reduce the surface tension of the solvent by 20 dyne/cm [Rosen, (1987)].

Effectiveness (Π_{cmc}):

The surface tension "γ_o" values at CMC were used to calculate values of surface pressure (effectiveness) form the following equation

$$\Pi_{cmc} = \gamma_o - \gamma_s$$

where γ_o is the surface tension measured for the pure water at the appropriate temperature and γ_s is the surface tension at CMC. The effectiveness of adsorption is an important factor to determine such properties of surfactant as foaming, wetting and emulsification, since tightly packed coherent interfacial films have very different interfacial properties than loosely packed, non coherent films [Rosen, (1987)].

Determination of Critical Micelle concentration (CMC)

CMC of the prepared surfactant was determined by the surface tension method [Hikota & Merguro (1970)]. In this method values of the surface tension obtained for various concentrations of aqueous solutions of the prepared surfactants were plotted vs. the corresponding concentrations

Maximum surface excess Γ_{max}

The surface excess concentration = surface concentration at surface saturation, the maximum surface excess Γ_{max} is a useful measure of the effectiveness of adsorption of the surfactant at the water-air interface, since it is the maximum value to which adsorption can attain.

$$\Gamma_{max} = \frac{1}{2.303\,RT} \left(\frac{\delta\gamma}{\delta\log c}\right)_T$$

where $R = 8.314$ Jmol^{-1}K^{-1}, T is absolute temperature, ($\delta\gamma$ /δ log C) is the slope of the γ vs. log C plot at room temperature [**Ammona & Magdi (2003)**].

A substance which lowers the surface tension is thus present excess at or near the surface, i.e. when the surface tension decreases with increasing the activity of the surfactant, Γ is positive.

Minimum surface Area (A$_{min}$)

A$_{min}$ is the minimum area per molecule of the prepared compounds at the interface was calculated from the following equation

$$A_{min} = \frac{10^{16}}{\Gamma_{max} N}$$

Where N is Avogadro's number and Γ_{max} is the maximum surface excess.

The standard free energies of micellization ΔG^{o}_{mic} and adsorption ΔG^{o}_{ads}

Understanding the process of micellization and adsorption are important for explanation of the effects of structural and environmental factors on the value of the CMC and for predicting the effects of new structural and environmental variations. Standard free energies of micellization ΔG^{o}_{mic}, and adsorption ΔG^{o}_{ads}, have played an important role in such understanding. The standard free energy of micellization and adsorption are given by:

$$\Delta G^{o}_{mic} = RT \ln(CMC)$$
$$\Delta G^{o}_{ads} = \Delta G^{o}_{mic} - 0.6023 \times \Pi_{CMC} A_{min}.$$

Analytical procedures for AAS analyses.
Copper, lead and mercury.

The reactions were carried out using a stoichiometric molar amount of the reagent with solutions of copper, lead and mercury. Each of the chelates was added separately to a series of (100) ml 50.00ppm (part-per-million) Cu^{+2}, pb^{+2} and Hg^{+2} solutions. A liquots (10) ml were collected then filtered at intervals of 1,6 and 20h following the addition of the chelating agents.

RESULTS AND DISCUSSION

The structure of the prepared chelate surfactants were confirmed by different means. FTIR series spectrometer (Table 2), elemental analysis (Table 3), HNMR and mass spectroscopy. The results were found to be compatible with the supposed structure.

Results of FTIR data

The chemical structures for surfactant samples were established according to FTIR (Table 2). The FTIR absorption spectra showed, generally absorption·band around $3400cm^{-1}$ indicating the presence of hydroxyl group, in addition to strong band at $1735cm^{-1}$ indicating the presence of ester group in the structure of these surfactants. Also the spectra revealed absorption band at $2800cm^{-1}$ indicating the presence of CH_2.

Results of elemental analysis data

A further confirmation of the prepared surfactants was given by elemental analyses. The data of elemental analyses are presented in Table 3. The data indicate that the calculated percentages of C, H and N are nearly close to the obtained measurements.

Results of proton nuclear magnetic resonance

The H^1NMR spectrum for some selective Chelating surfactants yielded: H^1NMR (DMSO-d_6)

surfactant	-CH$_2$-COO-	(CH$_2$-CH$_2$-O-)	CH$_2$-OOC	HC-S
II$_1$	2.5	3.5	3.9	2.9
II$_2$	2.5	3.5	4.3	2.9

Surface properties
Surface and interfacial tensions

Surface properties of the prepared chelating surfactants II$_{1-3}$ were measured and tabulated in Table 4.

The results in Table (4) indicate that surface and interfacial tensions of the prepared chelating surfactants II$_{1-3}$ decreased by increasing the number of moles of polyethylene glycol and decreasing the number of moles of anionic hydrophilic branch. This is because increasing of hydrophobic chain length and decreasing hydrophilic chain length decrease the aqueous solubility and cause migration of the

surfactant molecules from the bulk to the interface [Barry & El-Eini (1979) and Al-Sabagh, et al. (2000)].

Emulsifying Power

It is clear from Table (4) that all the prepared surfactants show adequate emulsifying power towards paraffin oil.

Critical micelle concentration

At this concentration, the surfactant monomers begin to aggregate in the bulk phase forming a sort of cluster known as micelle. The amount of surface tension attained at this concentration is defined as γ_{cmc}. The values of both CMC and γ_{cmc} are collected in Table 5 for anionic- nonionic hybrid surfactants. These data indicate that the values of the prepared surfactants II_{1-3} decrease by replacement of anionic branch by nonionic branch, this is due to the fact that in aqueous medium ionic surfactants have much higher CMC than nonionic surfactants.

In polyoxyethylene chains with anionic characteristics of carboxylic group, as polyoxyethylene content increases, anionic properties decrease and the materials become more like to nonionics in nature.

Effectiveness "Πcmc"

The most efficient surfactant is the one that gives the greatest lowering in surface tension for a critical micelle concentration (CMC). II_3 was found to be the most efficient (Table 5) because it achieved the maximum reduction of the surface tension at CMC (Fig. 1).

Efficiency "P_{C20}"

Values of efficiency of the prepared surfactants are shown in Table (5), the efficiency increases with increasing molar ratio of polyethylene glycol and decreasing the number of anionic branches. This is due to the fact that the replacement of anionic hydrophilic group by non ionic one results in a large increase in PC_{20} [Rosen, (1987)] as shown in Table (5).

Table (2): Elemental analysis for the prepared surfactants II $_{1-3}$.

Surfactants	M Wt	C%		H%		N%		S %	
		Calc	Found	Calc	Found	Calc	Found	Calc	Found
II$_1$	1121	32.33	32.51	6.01	6.15	6.24	6.28	8.56	8.60
II$_2$	1681	40.98	41.2	7.30	7.57	4.16	4.20	5.71	5.81
II$_3$	2241	45.30	45.70	7.95	8.10	3.12	3.15	4.28	4.32

Table (3): FTIR analysis results of the prepared surfactants II $_{1-3}$.

Surfactant	OH 3600-3200 cm^{-1}	C-O 1300-1350 cm^{-1}	CH2 2830-2975 cm^{-1}	C=O 1735-1750 cm^{-1}	C-S 2550-2600 cm^{-1}
II$_1$	+	+	+	+	+
II$_2$	+	+	+	+	+
II$_3$	+	+	+	+	+

Table (4): Surface properties of the prepared surfactants II $_{1-3}$.

Surfactant	Total number of P.E.G	Surface tension mN/m	Interfacial tension mN/m	Emulsifying power (min)
II$_1$	13.6	33	20	15
II$_2$	27.2	28	18	20
II$_3$	40.8	26	15	20

Table (5): Surface parameters of the prepared surfactants II $_{1-3}$.

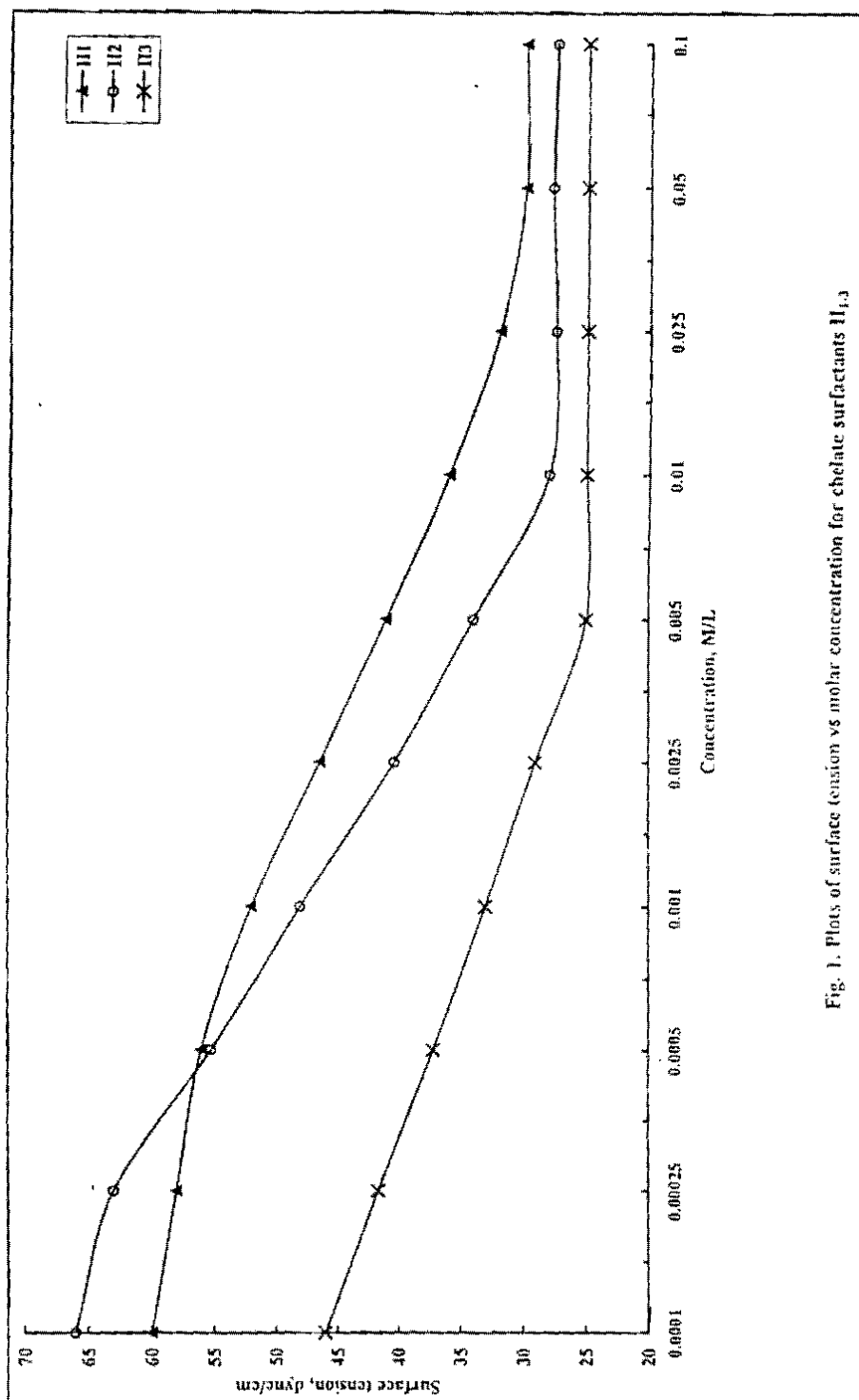| Surfactant	CMC $\times 10^{2}$ M/L	γ_{CMC} Dyne/cm	π_{CMC} Dyne/cm	Pc20 mole cm^2	Γ_{max} $\times 10^{10}$ Mole/cm^2	Amin (nm^2)	ΔG_{ads} kJ/mol.	ΔG_{mic} kJ/mol
II$_1$	0.02	30	41	3	1.7	1.2	-44.87	-19.36
II$_2$	0.01	28	43	3.1	0.08	1.1	-60.96	-22.79
II$_3$	0.005	25	46	4.3	1.3	1.22	-63-6	-16.22

Fig. 1. Plots of surface tension vs molar concentration for chelate surfactants II_{1-3}

Maximum surface excess Γ_{max}

It is evident from Table (5) that by increasing the number of moles of polyethylene glycol and decreasing the number of hydrophilic anionic moles, Γ_{max} increases, this contributes to the tendency of molecules to migrate to the water-air interface causing a consequent increase in Γ_{max} values.

Minimum area per molecule A_{min}

Results given in table (5) indicate that the consequent replacement of anionic hydrophilic moles leads to a decrease in A_{min} values. This is due to the crowdiness occurred at the interface as a result of increasing Γ_{max}.

The standard free energies of micellization ΔG°_{mic} and adsorption $\Delta G^\circ ads$.

It is evident from table (5) that the values of ΔG°_{mic} and ΔG°_{ads} are always negative indicating the spontaneous behaviors of these two processes, but there is more increase in negativity of ΔG°_{ads} compare with those of ΔG°_{mic} indicating the tendency of the molecules to be adsorbed at the interface.

Results of Cu^{+2}, pb^{+2} and Hg^{+2} from AAS data.

AAS results revealed that increasing the number of moles of poly ethylene glycol is associated with a decrease in the concentrations of the Cu^{+2}, Pb^{+2} and Hg^{-2} in the solution. This may be attributed to the fact that the replacement of the active hydrogen atom of carboxylic acid groups by oxyethylene units results in an increase in affinity of the chelate surfactant for metal ion [**Courtney, et al. (1953)**].

The resulting complexes are conveniently solubilized in the micelles of anionic-nonionic hybrid surfactant [**Giokas, (2002)**] and are thus separated from the bulk of aqueous phase, this replacement caused the decrease in CMC. Surfactants of lower CMC act as good chelating agents, because chelations is very slight at concentrations below CMC but abruptly rises beyond CMC. This may indicate that chelation is a micellar phenomenon.

Maximum removal of Cu^{+2} and Pb^{+2} by II₃, (Tables 6-8), (Figs.2-4) was observeal after 1 hour at neutral conditions. However, after 20

hours contact at neutral conditions, reasonably high removal of mercury (1.5 ppm) was determined.
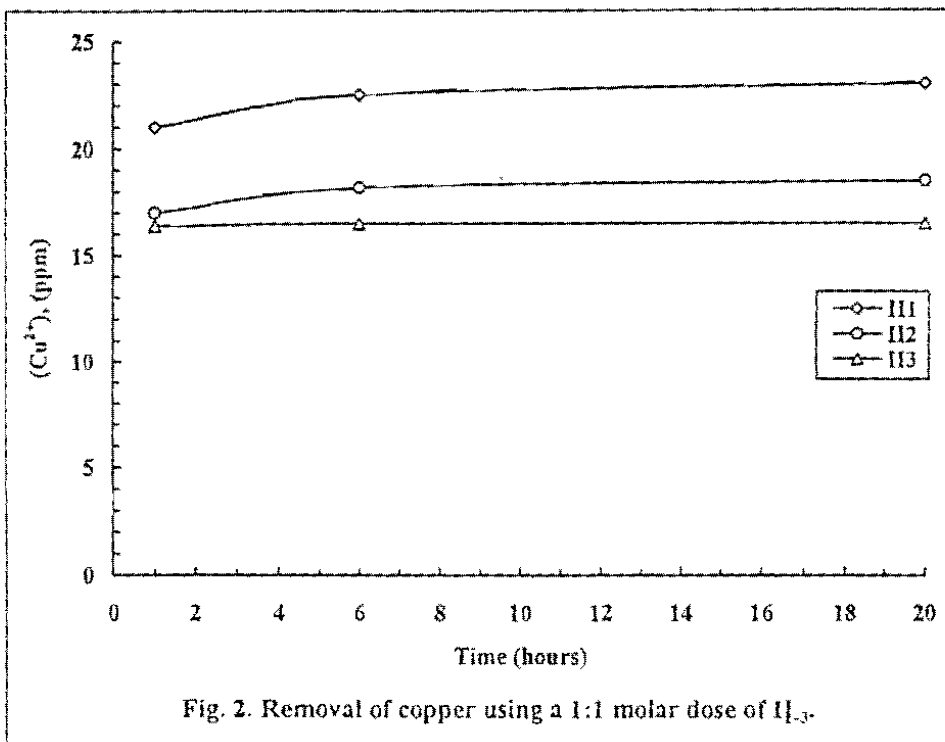
Table (6): AAS results of II_{1-3} Copper ions

Surfactant	Metal dose	Time of sample removal (h)	Final metal concentration (ppm)
II_1	Stoichiometric	1 6 20	21 22.5 23
II_2	Stoichiometric	1 6 20	17 18.2 17.5
II_3	Stoichiometric	1 6 20	16.4 16.5 16.5

Table (7): AAS results of II_{1-3} Lead ions

Surfactant	Metal dose	Time of sample removal (h)	Final metal concentration (ppm)
II_1	Stoichiometric	1 6 20	31 31.1 31
II_2	Stoichiometric	1 6 20	28.5 30 30.54
II_3	Stoichiometric	1 6 20	14.9 17 17.5

Table (8): AAS results of II_{1-3} Mercury ions

Surfactant	Metal dose	Time of sample removal (h)	Final metal concentration (ppm)
II_1	Stoichiometric	1 6 20	7.623 6.83 6.362
II_2	Stoichiometric	1 6 20	5.307 2.423 2.132
II_3	Stoichiometric	1 6 20	3.861 2.373 1.515

Fig. 2. Removal of copper using a 1:1 molar dose of II_3.

Fig. 3. Removal of lead using a 1:1 molar dose of II.3.

Fig. 4. Removal of mercury using a 1:1 molar dose of IL_3.
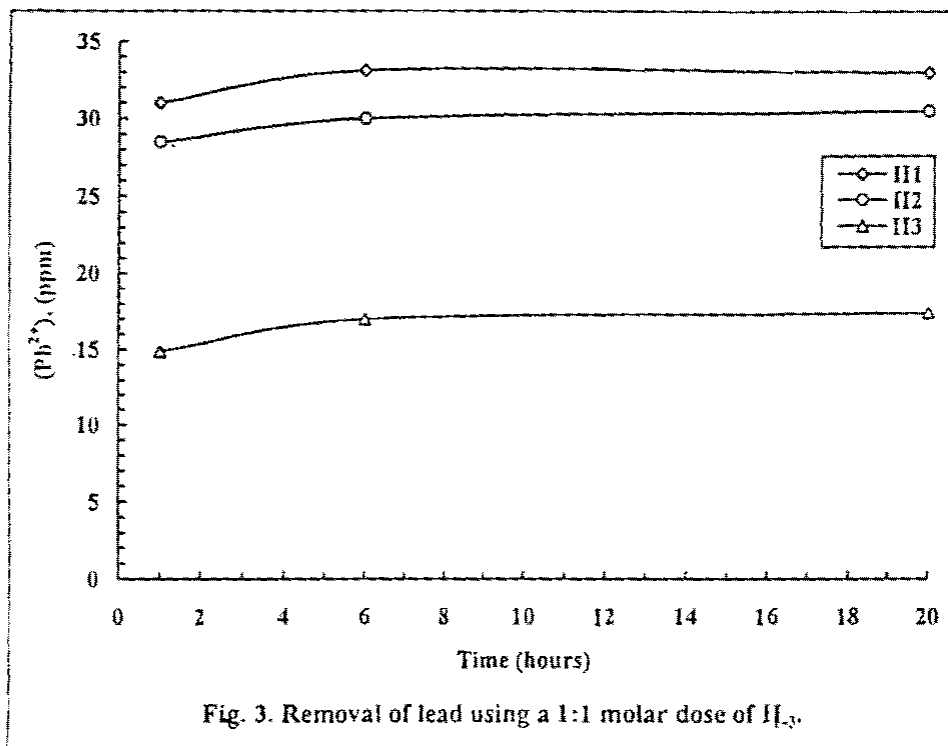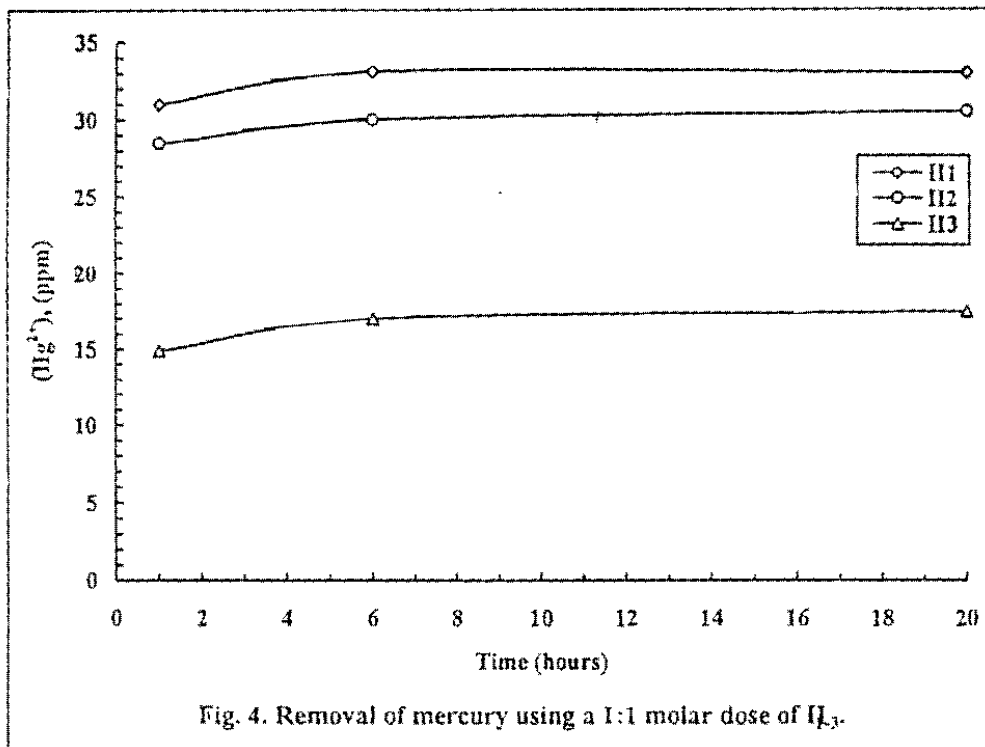
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تحضير وتقييم بعض المواد ذات النشاط السطحى وإستخدامها
كمخلبيات لبعض الفلزات الثقيلة

فــى هـذا البحـث تم تحضير مخلبيات مستحدثة بتفاعل إثيلين ثنائى أمين رباعى
حمــض الخلــيك مع ثلاثى مركبتوترايزين وبولى إثيلين جليكول. تم التعرف على الخواص
التركيبـية المميزة لهذه المخلبيات بالتحليل العنصرى طيف الأشعة الحمراء – الرنين الفورى
المغنطيســى وغـيرها. إتضـح أن هـذه المخلبيات تتحد مع عناصر النحاس ، الرصاص
والزئــبق – كمــا أن لهــا خــواص سطحية جيدة مثل التوتر السطحى ، كفاءة الأستحلاب ،
التركيز الميسيلى الحرج وغيرها.