

Use of some hydrazine derivatives for the separation of mercury(II) from aqueous solutions by flotation technique

S E Ghazy, T H Rakha, E M El-Kady & A A El-Asmy

Chemistry Department, Faculty of Science, Mansoura University, P.O. Box 66, Mansoura, Egypt

Received 4 October 1999; accepted 15 May 2000

Some hydrazine derivatives viz: pyridinium chloride acetylhydrazine (PAH), 1-acetylpyridinium chloride-4-phenylthiosemicarbazide (APPT), 1-acetylpyridinium chloride-*o*-hydroxyacetophenone hydrazone (APHH), trimethylammonium chloride acetylhydrazine (TAH), 1-acetyltrimethylammonium chloride-*o*-hydroxyacetophenone hydrazone (ATHH) and 1-acetyltrimethylammonium chloride diacetylmonoxime hydrazone (ATDH) are investigated as floating agents for the separation of mercury (II) using oleic acid surfactant. Of these, APPT is the most suitable for giving maximum flotation efficiency (~100%). Surfactant, metal ion and ligand concentrations, ionic strength, foreign ions, pH and temperature are examined as important parameters affecting the floatability of Hg(II). The procedure is successfully applied to recover Hg(II) from some natural water samples with a relative standard deviation of 1.6%. Moreover, the mechanism of flotation is suggested based on some physical and chemical studies on the solid complexes isolated from aqueous and scum layers.

Anthropomorphic redistribution of mercurials has ravaged a substantial portion of our planet. Japan, Sweden, Canada, the Great Lakes, Iraq, Pakistan, Ghana and Guatemala form a partial listing of contamination sites and provide a historical basis to review some of the teleost studies¹. Mercury is considered to be a serious heavy metal pollutant². Hg-induced toxicity is related to differences in species, chemical form, specimen size and temperature, as well as other factors¹. Hg(II) can be methylated to (CH₃)₂Hg and CH₃Hg⁺ and there are a number of factors controlling the amount of methylation^{3,4}. Therefore, the longer the divalent inorganic mercurials remain in the environment, the more problematic the Hg contamination becomes, because of the lipophilicity of the product-organic alkylmercury salt. The safety level for Hg in sea foods (0.5 ppm) is exceeded in many places in the world¹. According to the World Health Organization, provisional maximum intake for Hg in human is 0.3 mg / person / week, of which not more than 0.2 mg should be CH₃Hg⁺ species⁵. Since the majority (often 100%) of Hg in muscles is CH₃Hg⁺ species⁶, little safety margin exists.

For the foregoing reasons, the separation and/or determination of Hg(II) from natural waters are vital processes. Various techniques for the separation and/or preconcentration of metal ions prior to their determination are available which include volatilization, liquid-liquid extraction, selective

dissolution, sorption, ion exchange, liq chromatography, flotation, freezing and zone melting^{2,7}. Of these, flotation technique has particular merit in providing quick, quantitative & selective separation under proper conditions; therefore is the choice for this investigation.

Although some work has been carried out for flotation of Hg(II) from aqueous solutions, wastes & natural waters^{2,8-14}, no attention has been paid towards the use of hydrazine derivatives in this respect. The objective of the present work is to extend application of flotation technique to separate Hg from the aforementioned solutions using PAH, APPT, APHH, TAH, ATHH, ATDH and oleic acid surfactant under the optimum conditions.

Experimental Procedure

Reagents-Unless otherwise stated, all chemicals used in this investigation were of analytical grade. Oleic acid (HOL) surfactant was used directly received. Its stock solution, 3.36×10^{-2} mol/L, was prepared from food grade chemical with specific gravity 0.895 (J.T. Baker Chemical Co.) by dispersing 20 mL in 1 L kerosene. Mercuric chloride (HgCl₂) stock solution, 1×10^{-2} mol/L was prepared in double distilled water. Girard's reagent P (PAH) and Girard's reagent T (TAH) stock solutions, 1×10^{-3} mol/L, each were prepared without purification by dissolving the calculated amount in double distilled water. The stock solutions of the ligands APPT, APHH, ATHH and

Table 1—Effect of some foreign ions on the floatability of 6×10^{-5} mol/L (12 mg/L) Hg(II) using 6×10^{-4} mol/L APPT and 1×10^{-3} mol/L HOL at pH 6.8.

Foreign ion	Concentration ($\times 10^3$ mg/L)*	Floatability (%)	Foreign ion	Concentration ($\times 10^3$ mg/L)*	Floatability (%)
Ag ⁺	21.8	99.9	EDTA	10.0	99.8
Ba ²⁺	13.7	99.8	SO ₄ ²⁻	9.6	99.5
Sn ²⁺	12.0	99.9	Oxalate or citrate	9.0	99.9
Co ²⁺	6.0	100.0	SO ₃ ²⁻	8.0	100.0
K ⁺	4.0	100.0	SCN ⁻ or PO ₄ ³⁻	4.0	99.8
Mg ²⁺	3.9	100.0	Cl ⁻ , Br ⁻ or I ⁻	3.6	99.6
Al ³⁺	2.7	99.9	Cr ₂ O ₇ ²⁻	2.2	99.7
Na ⁺	2.3	100.0	B ₄ O ₇ ²⁻	1.6	99.0
Zr ⁴⁺	0.5	99.5	S ₂ O ₃ ²⁻	0.7	99.9
Ni ²⁺ or Cu ²⁺	0.3	99.7	HCO ₃ ⁻	0.6	99.8
Mn ²⁺	0.2	99.7	IO ₃ ⁻	0.2	99.5
Ca ²⁺ , Sr ²⁺	0.1	99.8	CO ₃ ²⁻	0.1	97.8
Cd ²⁺ or Fe ³⁺					
Cr ³⁺	0.01	99.5			

* This concentration represents the maximum value of the foreign ion above which the floatability of Hg(II) is highly affected.

Table 2—Recovery of Hg(II) added to water samples using 6×10^{-4} mol/L APPT and 1×10^{-3} mol/L HOL at pH 6.8.

Types of water (location)	Hg(II) added (mg/L)	Recovery of Hg(II) (%)*
Distilled water	12	100
	15	100
Drinking water (Mansoura)	12	99.9
	15	99.9
Nile water (Mansoura)	12	99.8
	15	99.7
Sea water (Alexandria)	12	99.6
	15	99.6
Sea water (Gamasa)	12	99.7
	15	99.6
Lake water (Manzalah)	12	99.1
	15	99.0
Underground water (Nawasa El-Bahe)	12	99.0
	15	98.5

* The mean of seven replicate analysis.

ATDH, 1×10^{-2} mol/L. each, were prepared in double distilled water. The solids of these ligands were prepared by slowly adding phenylisothiocyanate (13.5 mL), *o*-hydroxyacetophenone (13 mL) and/or diacetylmonoxime (10 g) to a solution of Girard's reagent P (18.6 g) or T (13.2 g) in absolute ethanol. The mixture was refluxed on a water bath for a fixed time (15–120 min) depending on the reaction mixture. The product thus obtained was crystallized several times from absolute ethanol and dried in a vacuum desiccator over anhydrous CaCl₂. The purity of the ligands was checked by elemental analysis and IR spectra.

Apparatus—The flotation cell (a cylindrical tube of 29 cm length and 1.5 cm inner diameter, provided with a stopcock at the bottom) was as mentioned¹⁵ previously. The infrared spectra of the ligands and their Hg(II) complexes were recorded on MATTSON 5000 FTIR Spectrometer using KBr disc. The pH measurements were determined using HANNA Instruments 8519 digital pH meter. Thermal measurements (TG and DTG) were recorded in a nitrogen atmosphere between 20 and 800 °C, using Shimadzu Thermogravimetric Analyzer TGA-50 with α -Al₂O₃ as a reference material. Carbon and hydrogen contents of the solid complexes were carried out in the Microanalytical Unit of Mansoura University. Hg(II) was determined complexo-metrically using semixylenol orange (SXO) as indicator¹⁶.

Procedure—A suitable concentration of Hg(II), specified for each test, was mixed with one of the investigated hydrazine derivatives followed by 10 mL double distilled water. The pH of the solution, if necessary, was controlled to the optimum value using HCl and/or NaOH; fortunately the optimum pH value, ~6.8, was obtained by direct addition of the reagents. The solution was transferred quantitatively to the flotation cell and made-up to 20 mL with double distilled water. The cell was shaken well for few seconds, to ensure complexation. To the above solution, 3 mL of HOL (with definite concentration) was added. The cell was then turned upside down 20 times by hand. After 5 min standing, to complete flotation, the concentration of Hg(II) in the mother liquor or in the scum is determined complexo-metrically¹⁶.

The floatability ($F\%$) of Hg(II) was calculated from its concentration in the mother liquor according to the relation

$$F = 1 - C_1 / C_2 \times 100\%$$

where C_1 and C_2 denote the initial and final concentrations, respectively.

Alternatively, the concentration of Hg(II) in the scum (C_2) can be obtained by filtering the precipitate in the scum and washing it with distilled water. The precipitate is then dissolved in 5 mL concentrated HNO_3 , heating to dryness, adding 10 mL hot double distilled water and filtering the solution for Hg(II) determination. The flotation efficiency ($F\%$) can be calculated as,

$$F = C_1 / C_2 \times 100\%$$

where C_1 and C_2 denote the initial and the scum concentration of Hg(II).

Results and Discussion

Selection of collecting agent- The collecting ability of some hydrazine derivatives such as PAH, TAH, APPT, APHH, ATHH or ATDH towards Hg(II) was examined. The experiments take into consideration the effect of variable concentrations of the reagents on the floatability of 8×10^{-5} mol/L Hg(II) using 1×10^{-3} mol/L, HOL at pH 6.8. It was noted that the maximum flotation efficiency ranges from 60 to 80% which was obtained in the presence of PAH, TAH, APHH, ATHH or ATDH. In the case of APPT, the floatability of Hg(II) increases gradually reaching its maximum value ($\sim 100\%$) at a 1:2 molar ratio of Hg(II): APPT and remains constant with increasing concentration of APPT; this maximum efficiency may be due to the presence of thione group ($\text{C}=\text{S}$) in APPT only. Therefore, the higher concentration of APPT has no adverse effect on Hg(II) flotation, which makes its separation from unknown or real samples easier. A concentration of APPT which equals ten-folds of Hg(II) is used in the recommended procedure.

Effects of metal ion concentration- Attempts to float different concentrations of Hg(II) using 1×10^{-3} mol/L of hydrazine derivatives and 1×10^{-3} mol/L HOL, at pH 6.8 were carried out. Close inspection of the results obtained showed that APPT is the most superior among all the other hydrazine derivatives, giving $\sim 100\%$ flotation efficiency. This maximum flotation efficiency remains constant whenever the concentration of APPT is twice that of Hg(II) or more. The flotation begins to decrease when Hg(II): APPT ratio is more than 1:2.

Effect of pH on collection and flotation- A series

of experiments were conducted to investigate the relation between the floatability of 6×10^{-5} mol/L Hg(II) and pH using 6×10^{-4} mol/L of each of the hydrazine derivatives and 1×10^{-2} mol/L HOL. The results are shown in Fig. 1. It is clear that the floatability of Hg(II) increases gradually, reaching its maximum value in the pH range 5-7 for all the examined hydrazines. Of these reagents only APPT gives $\sim 100\%$ flotation efficiency. Above a pH value of 7, the efficiency decreases, which may be attributed to the excessive foam formed.

In order to investigate the relation between the stoichiometric ratio (Hg(II): APPT) and the pH, another series of experiments were carried out using different ratios at variable pH values. The maximum flotation efficiency ($\sim 100\%$) is obtained at ratios 1:2, 1:3 and 1:4 (Hg(II): APPT) in the same pH range 5-7, which is in good agreement with the other data obtained. So, for assured functioning, a concentration of APPT which is ten times that of Hg(II) and pH 6.8 (fortunately obtained from direct addition of the reagents) are selected in the recommended procedure.

Effect of surfactant concentration- Trials were conducted to float 6×10^{-5} mol/L Hg(II) using hydrazine derivatives (6×10^{-4} mol/L, each) and different concentrations of HOL at pH 6.8. It was found that the flotation efficiency increases slightly on increasing the concentration of HOL and gives its maximum value ($\sim 100\%$ only for APPT) at a wide concentration range of 1×10^{-4} - 1×10^{-2} mol/L HOL. At

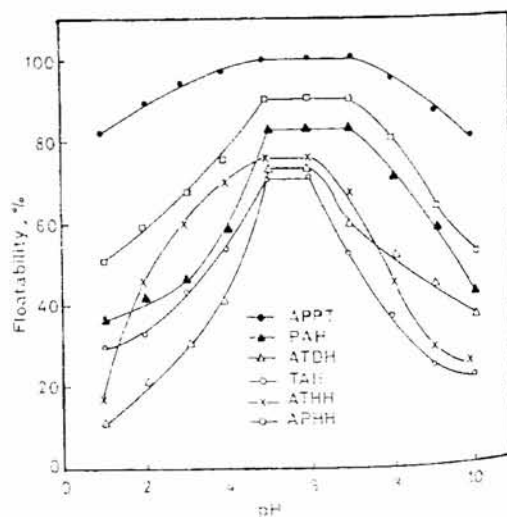


Fig. 1—Effect of pH on the floatability of 6×10^{-5} mol/L Hg(II) using 6×10^{-4} mol/L of each hydrazine derivative and 1×10^{-2} mol/L HOL.

Table 3—Some physical and chemical data of the isolated solid complexes

Property and measurements		APPT	Hg(APPT-H) ₂	Hg(APPT)Cl ₂ ·3H ₂ O
Colour		White	White	Yellowish white
M.P., °C		161	208	203
Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)		54	52	70
Element	C	52.3(51.8)	39.8(39.6)	22.2(22.0)
Analysis	H	4.4(4.6)	3.3(3.2)	(3.2(3.0)
% Calc (Found)	Hg	-	23.8(23.4)	30.9(30.7)
	Cl	11.0(11.1)	8.4(8.1)	16.4(17.0)
IR bands	ν(CO)	1717	-	1700
	ν(CS)	780	780	780
	ν(N ¹ H)	3033	-	3030
	ν(N ² H)	3136	3110	3150
	ν(C=N)	-	1630	-
	ν(M-O)	-	383	380
	ν(M-N)	-	450	435
Weight loss				
in TG	71-200°C		Stable	8.3(7.3) ^c
Analysis	200-305°C		32.3(33.1) ^a	31.9(30.7) ^d
% Calc (Found)	305-375°C		38.6(38.3) ^b	24.8(24.8) ^e

Weight loss due to liberation of: a-(C₆H₅NHCS)₂, b-(C₇H₇N₃)₂O+Cl₂, c-3H₂O, d- Cl₂ + C₆H₅NHCS; e- C₆H₅NCH₂CNIHIL.

concentrations, more than 1×10^{-2} mol/L HOL, the efficiency decreases owing to the formation of micelles and the HOL surfactant becomes firmly attached to the glass walls of the flotation cell. Therefore 1×10^{-3} mol/L HOL is the choice for the other flotation measurements. From the foregoing data, 6×10^{-5} mol/L Hg(II), 6×10^{-4} mol/L APPT, 1×10^{-3} mol/L HOL and pH 6.8 are the optimum conditions which will be used throughout this investigation.

Effect of temperature—The flotation efficiency of Hg(II), under the recommended conditions, has maximum value (~ 100 %) in the temperature range 20-35 °C. Increase in temperature decreases the floatability of Hg-APPT precipitate by HOL surfactant. This may be attributed to the fact that an increase of temperature may increase the solubility of the precipitate and the instability of the foam giving rise to partial dissolution of the precipitate and insufficient foam consistency to hold up the precipitate.

Effect of ionic strength—The effect of ionic strength (covering a wide concentration range from 1×10^{-3} to 1×10^{-1} mol/L of each salt) on the floatability of 6×10^{-5} mol/L Hg(II) using 6×10^{-4} mol/L APPT and 1×10^{-3} mol/L HOL at pH 6.8 was investigated. The salts (namely: NaCl, KCl, Na₂SO₄ and CaCl₂) added to the flotation medium contain cations and anions,

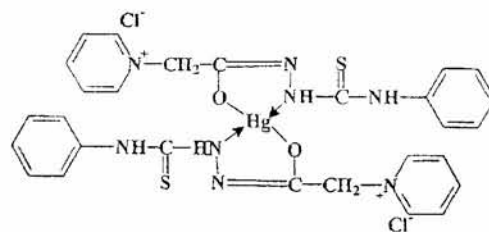
nearly resembling to those present in natural water. The results obtained show that all the salts have no effect on flotation efficiency. Only CaCl₂ decreases the flotation efficiency owing to the formation of calcium oleate resulting in a decrease of the concentration of oleic acid surfactant needed for flotation. The adverse effect of CaCl₂ can be overcome by adding slight excess of oleic acid surfactant.

Effect of foreign ions—In order to assess possible applications of this study in the separation processes, the effects of diverse ions on the floatability of Hg(II) were investigated by adding known amounts of the ion in question, to a solution containing 12 mg/L of Hg(II) and following the recommended procedure. The results are summarized in Table 1. A close inspection of the table shows that Cr³⁺ has a harmful interfering effect, which may be due to the formation of higher stable complex with APPT and thus decreasing its concentration available for Hg(II) flotation. The addition of an excess concentration from APPT overcomes Cr(III) interference. Ni²⁺, Cu²⁺, Ca²⁺, Sr²⁺, Cd²⁺ or Fe³⁺ may only interfere at higher concentrations. The interference which may be due to the formation of insoluble oleates of these interferents was overcome by addition of slight excess of oleic acid surfactant or few drops of one molar

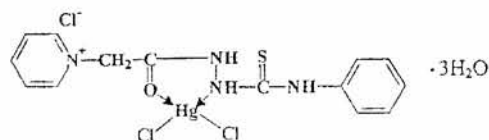
solution of EDTA or NTA. This agrees well with the literature data¹⁷ that heavy metal and polyvalent metal ions form precipitates with anionic surfactants, curds or lime-soap, that reduce the effective concentration of surfactant and adversely affect performance. If the hardness of water is not too much, an excess of anionic surfactant can be used to disperse the curd and render it innocuous. Organic sequestering agents such as EDTA or trinitriloacetic acid (NTA) tie up heavy metal ions in non-ionizing complexes and prevent the formation of soap curds. This makes it possible to use anionic surfactant in hard water. Also, higher concentrations of some investigated anions may interfere, which may be attributed to a competition between them and the ligand (APPT) towards Hg(II).

Application—In order to evaluate the capability of the flotation procedure for the recovery of Hg(II) from water, various types of water samples were selected. The selection of these samples was done in a way as to provide a wide variety of sample matrices characterized by different types of interferents. 12 or 15 mg of Hg(II) were added to 20 mL of prefiltered water samples and floated under the optimum conditions. The data presented in Table 2 show that satisfactory recoveries of Hg(II) are obtained. The percent relative standard deviation of seven replicate analysis of the mentioned samples (Table 2) is 1.6 %.

Flotation mechanism—In order to propose a mechanism for the flotation of Hg(II), the complexes formed on the reaction between APPT and HgCl₂ were isolated in the absence and presence of HOL surfactant. A comparison between the behaviour of the two complexes gives an insight into their coordination sites and their structures. Inspection of the data (Table 3) obtained from elemental analysis, IR and thermal studies indicates the formation of Hg(APPT)₂ and Hg(APPT)Cl₂·3H₂O in the aqueous and scum layers (Structures I and II), respectively. Since, the IR spectrum of the complex isolated from the scum has no oleic acid absorption bands, it is suggested that HOL may combine weakly with Hg(II) complex through physical or hydrogen bonds and the aggregates then float to the surface with the aid of air bubbles.



Structure (I)



Structure (II)

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