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Selective Liquid–Liquid Extraction of Mercuric Ions by Octyl Methane Sulfonamide

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ABSTRACT

N-octyl methane sulfonamide (OMSA) has been demonstrated to be a very efficient reagent for selective extraction of Hg(II) ions, from aqueous solutions. The extraction bases on rapid reaction of OMSA with Hg(II) ions yielding mono and disulfonamido mercury compounds in ordinary conditions. Solubility of OMSA and its mercury compounds in 2-ethyl hexanol provide a clear-cut phase separation in the extraction. The solution of OMSA in 2-ethyl hexanol (0.4 mol L^{-1}) is able to extract 82.2% of mercuric-acetate (0.4 mol L^{-1}) in non-buffered conditions. Although the process depends on the nature of accompanying anions, the distribution coefficient is reasonably high ($k_d \geq 1.27$) even in the presence of chloride ions. The extraction is strictly selective and the presence of Cd(II), Zn(II), Pb(II) do not bring any interference.

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The extraction system works in moderate concentrations. Extracted mercury in the organic phase can be recovered by back-extraction with concentrated HCl or H₂SO₄ solutions. After acid treatment, the organic solution of OMSA becomes regenerated without losing its activity due to reasonable hydrolytic stability of the sulfonamide linkage and it can be recycled for further extractions.

Key Words: Liquid–liquid extraction; Selective mercury extraction; Octyl methane sulfonamide.

INTRODUCTION

Selective extraction of metal ions has been one of the most important tasks both in laboratory and in industry. Since the pioneering study of Nishide and Tsuchida,^[1] metal templated cross-linked polymer sorbents have been used for selective separation of metal ions. Although this approach is presented as the common method, selectivity of the sorbent is directly proportional to the cross-linking density which greatly reduces the sorption capacity. Even in that case, a strict selectivity has never been attained so far. And the method needs further improvements to reach reasonable selectivities. The best method of the selective separation is of course to use extractants with special groups having exceptional affinity to any desired entity to be separated. But this is rarely possible. Nevertheless, mercuric ion is the exception. It shows unusual affinities toward some organic functional groups such as thioethers and amides. Based on greater affinity of mercury toward thioether function, selective separation of mercury has been achieved using polymer supported thioethers.^[2] However, due to the electron donating nature of thioether group, it can also react with many heavy metal ions to some extents. And the separation is not entirely selective. In a similar study, polymer pendant crownthioethers have been used for selective removal of Hg(II) ions, with 95% efficiency from highly acidic solutions in pH:0–3 range. Stripping of bound mercury has been achieved by the solution of diphenylthiocarbazone in CHCl₃.^[3] Also triisobutylphosphine sulfide on silica gel surface has been used for chromatographic separation of mercury from binary mixtures.^[4] Additionally, solvent extraction of mercury by cyclic thioamides such as w-thiocaprolactam dissolved in chloroform has been achieved even in concentrated HCl solutions.^[5] In a related study calix[4]arenes with 2-methylthioethoxy substitutions have been used for extraction of some heavy metal ions including Hg(II).^[6] Some aliphatic

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monoamines with two or tetrathioether groups have been claimed to be efficient in liquid–liquid extraction of Ag(I), Cu(I), Pd(II), and Hg(II) ions selectively over some other metal ions.^[7] In another study 1-naphthylthiocarbamide in CHCl₃ has been used for selective extraction of mercury in concentrated acid solutions.^[8]

Amide group also is susceptible to Hg(II) ions. Amide group is known to react with Hg(II) to give covalent bonds in ordinary conditions and mono and diamido mercury compounds form rapidly. By contrast, amide nitrogen does not form a coordinative bond with other transition metal ions in ordinary conditions due to reduced electron donating behavior of the amide nitrogen. As a result, sorbents, with amide groups, can be considered as mercury specific. There appear only limited reports on the use of amide groups, in the literature, for selective extraction of mercury. Polymers obtained by ring opening metathesis polymerization of norbornene containing 2-pyridyl and amide groups have been described as selective extracting reagent for Hg(II) and Pd(II).^[9] Based on the exceptional reactivity of amide groups, in our previous studies, we have demonstrated that cross-linked polyacrylamide^[10] and its graft copolymers with cotton cellulose^[11] show very high mercury sorption capabilities in ordinary conditions.

In the present study, this analogy has been extended to liquid–liquid extraction of mercuric ions. For this purpose N-octyl methane sulfonamide (OMSA) has been prepared and its solution in 2-ethyl hexanol has been demonstrated to be specific for the mercury extraction. The advantage of sulfonamides over carbonamides is their reasonable high hydrolytic stability which provides processing in highly acidic or basic conditions. In the study the mercury extraction and regeneration of the extracting agent have been investigated in various conditions.

EXPERIMENTAL

Material

All the chemicals used were analytical grade commercial products. They were used as supplied (methanesulfonyl chloride—Fluka, octyl amine—E.Merck, 2-ethyl hexanol—Aldrich, Mercuric salts—E.Merck).

Preparation of n-Octyl Methane Sulfonamide (OMSA)

33.1 ml (0.2 mole) octyl amine, 17.0 ml (0.2 mole) pyridine (as HCl scavenger) and 35 ml 1-methyl 2-pyrrolidinone (NMP) were mixed in a 250 ml volume of flask in ice-bath. To the stirred solution 16.0 ml (0.206 mole) methane sulfonyl chloride was added dropwise. Stirring was continued at room temperature for 3 h and heated at 80°C for 1 h. The reaction content was poured into 500 ml water. White precipitate was filtered and washed with water. The crude product was recrystallized from 100 ml acetic acid–water (1:1) mixture. White crystalline product was filtered and dried under vacuum at room temperature for 24 h. Overall yield 38.6 g (93.2%) mp:48.6°C.

Elementary analysis: Calculated for $C_9H_{21}NO_2S$ %, (found %) C: 52.17% (52.7); H: 10.14% (10.2); N: 6.76% (6.60).

1H -NMR spectra (Bruker 250 MHz NMR-Spectrometer): δ (in DMSO- d_6 with TMS internal standart); 6.9 ppm (t, D_2O exchangeable, 1H, N–H), 2.9 ppm (t, 2H, N–CH $_2$ –), 2.85 ppm (s, 3H, –O $_2$ S–CH $_3$), 0.8–1.5 ppm (multiplets, 15H, aliphatic protons).

The product is soluble in 2-ethyl hexanol, dimethyl formamide (DMF), cyclohexanol, acetic acid, dimetyl sulfoxide (DMSO) and insoluble in water.

Liquid–Liquid Extraction of Hg(II) Ions

Extraction experiments were carried out in a 100 ml volume of separatory funnel. Thus, 2.07 g (0.01 mole) octyl methane sulfonamide in 25 ml 2-ethyl hexanol were mixed and shaken with 25 ml of aqueous Hg(II) solutions in different concentrations. The equilibrium was established by vigorous shaking for 5 min. The aqueous phase was separated by means of the separatory funnel. Hg(II) ions remaining unreacted in the aqueous phase was determined by colorimetric method using diphenylcarbazide as color reagent.^[12] Hg(CH $_3$ COO) $_2$, Hg(NO $_3$) $_2$ and HgCl $_2$ salts were used to inspect effect of the counter anions. The results found were collected in Table 1.

Chlorine Analysis

After extraction from 25 ml of HgCl $_2$ (0.25 mol L $^{-1}$), chloride ion concentration of the aqueous solution was determined as follows: 10 ml of the aqueous solution was interacted with 5 ml of 5 M NaOH solution to precipitate mercury as HgO. The mixture was heated for 15 min. in water bath.

**Mercuric Ion Extraction****205****Table 1.** Effect of counter anions in the mercury extraction.

Mercuric salt	Initial conc. (M)	Conc. of OMSA (M)	Theoretical capacity (mmol)	Extracted Hg(II) (mmol)	Extraction ^a coefficient	Recovered ^b Hg(II) by acid stripping (mmol)
HgCl ₂	0.25	0.25	6.25	3.51	0.560	3.30
Hg(NO ₃) ₂	0.40	0.40	10.0	7.76	0.776	7.47
Hg(CH ₃ COO) ₂	0.40	0.40	10.0	8.22	0.822	8.03

^a Using 25 ml OMSA solution in 2-ethyl hexanol and 25 ml of mercuric solution.^b Recovered mercury with 6 M HCl solution (25 ml).

The yellowish-red precipitate was filtered and washed with distilled water. The filtrate was made up 25 ml and neutralized with 1 M HNO₃ solution. 10 ml of 2 M AgNO₃ solution was added to precipitate AgCl. White precipitate was collected by filtration and dried at 40°C for 24 h. The silver chloride weighed 0.671 g which corresponds to 0.468 M chloride ion concentration in the final aqueous solution.

pH Dependent Hg(II) Extractions

The same extraction experiments were repeated in buffered solutions at pH 1.0; 2.1; 3.10 and 4.05 (prepared by appropriate combination of NaCl–HCl solutions in 0.1 M concentrations) by using 0.4 M mercuric acetate solution (Table 2). The unreacted mercury concentrations were determined colorimetrically as described above.

Table 2. Effect of foreign ions in extraction of HgCl₂.

Foreign ion	Accompanying anion	Initial conc. (mol L ⁻¹)	Final Conc. (mol L ⁻¹)	HgCl ₂ initial conc. (mol L ⁻¹)	HgCl ₂ final conc. (mol L ⁻¹)
Fe(III)	Cl ⁻	0.50	0.482	0.25	0.107
Zn(II)	Cl ⁻	0.50	0.487	0.25	0.1076
Cd(II)	Cl ⁻	0.50	0.498	0.25	0.109
Pb(II)	CH ₃ COO ⁻	0.50	0.500	0.25	0.024 ^a
None	—	—	—	0.25	0.1076

^a With mercuric acetate.

Mercury Extraction in Presence of Foreign Ions

In order to examine the effect of some common metal ions such as Cd(II), Fe(II), Zn(II), and Pb(II) the extraction experiments were repeated in the presence of those ions with 0.5 mol L^{-1} concentrations. But, beforehand, extractability of these ions was studied separately by shaking the extractant solution with the foreign ion solutions (0.5 mol L^{-1}) alone. Analyses of CdCl_2 , FeCl_3 , ZnCl_2 , and $\text{Pb}(\text{CH}_3\text{COO})_2$ solutions were carried out by complexometric titrations with EDTA as described in the literature.^[13] In those experiments concentration of Cd(II), Pb(II) were found to be almost the same with those of the initial solutions. Zn(II) and Fe(III) were slightly less (0.485 and 0.489 mol L^{-1} respectively) than those of the starting solutions (0.5 mol L^{-1}). Competitive experiments were conducted in binary mixtures of mercury with one of the above salts. Different analytical procedures were employed for analyses of Hg(II) remaining in the aqueous phase. The diphenyl carbazide method does not work in the presence of those ions, due to the fact that it produces colored complexes also with the other metal ions except Cd(II). Analyses of Hg(II)–Pb(II), Hg(II)–Zn(II), Hg(II)–Fe(III), binary mixtures were performed by general procedure given in the literature.^[14] The results were listed in Table 2.

Effect of NaCl Concentration

Many anions of Hg(II) can be replaced with chloride ions, due to high-formation constant of HgCl_2 . Therefore presence of chloride ions is expected to affect the mercury extraction. To investigate the effect of chloride ions the extraction experiments were performed with mixed HgCl_2 –NaCl solutions in different concentrations (0.01 – 1.5 mol L^{-1}) (Fig. 2).

Regeneration and Recycling of the Extractant

Regeneration of the mercury-loaded extract phase was performed using concentrated HCl or H_2SO_4 solutions. For this purpose 25 ml of the extract phase were separated by separatory funnel and shaken with 25 ml of concentrated acid solutions with different concentrations to release mercury from OMSA. The mercury transferred to the aqueous phase was assayed colorimetrically. Analytical results are shown in Table 3.

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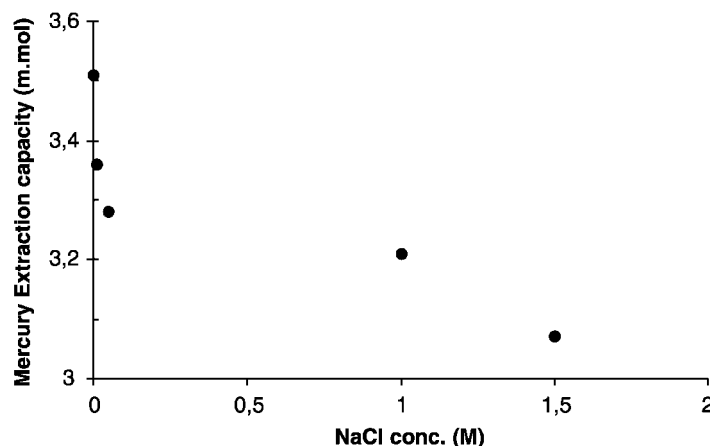


Figure 2. Variation of mercury extraction capacity of 25 ml OMSA solution (0.25 mol L^{-1}) with sodium chloride concentration (from 25 ml of 0.25 mol L^{-1} HgCl_2 solutions).

RESULTS AND DISCUSSION

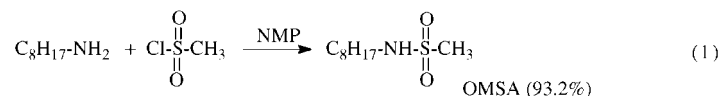
N-octyl methanesulfonamide (OMSA) was synthesized for selective mercury extraction simply by interaction of n-octylamine with methane sulfonyl chloride (Scheme 1).

Structure of OMSA has been confirmed by $^1\text{H-NMR}$ and elementary analysis. Recrystallization from acetic acid–water (1:1 v/v) mixture gives

Table 3. Recovered mercury from organic phase (loaded with HgCl_2) (25 ml) by acid leaching.

Acid	Acid conc.	Loaded ^a (mmol)	Recovered (mmol)	Percentage stripping (%)
H ₂ SO ₄	10% (v/v)	3.51	1.3	37.0
H ₂ SO ₄	20% (v/v)	3.51	2.0	57.0
H ₂ SO ₄	40% (v/v)	3.51	3.1	88.3
HCl	1 M	3.51	1.7	49.4
HCl	2 M	3.51	1.9	54.1
HCl	3 M	3.51	2.3	65.5
HCl	6 M	3.51	3.3	94.0

^aLoaded mercury from 25 ml of 0.25 M HgCl_2 solution.



NMP : N-methyl , 2-pyrrolidinone

Scheme 1.

product which is free of the octylamine. In its $^1\text{H-NMR}$ spectrum, the signal observed at 6.9 ppm indicates N—H proton which is replaceable with D_2O . The characteristic methyl group singlet appears at 2.85 ppm and methylene protons adjacent to nitrogen at 2.9 ppm. All the other aliphatic proton peaks lie in 0.8–1.5 ppm range.

Mercury Binding

This compound, OMSA, has been considered as a mercury specific extracting agent. The long aliphatic chain is expected to render it soluble in the organic solvents. OMSA is soluble in many organic solvents such as CHCl_3 , cyclohexanol, DMF, 2-methyl pyrrolidone, and 2-ethyl hexanol. The latter is an especially suitable solvent for the extraction, due to its nonvolatility. The reagent OMSA is expected to bind Hg(II) ions by forming mono or disulfonamido compound. The reaction must be specific. All amide compounds are known to react with mercury to give covalent linkage through nitrogen atoms of the amide groups in ordinary conditions. For instance, reaction of benzamide with Hg(II) has been proposed as gravimetric method for mercury analysis.^[15] Since the amide nitrogen is lack of electron donating character, amide groups are not capable of forming coordinative bond. Hence, these do not form complexes with transition metal ions in ordinary conditions. This is the key point of their mercury specificity. The sulfonamides have a special advantage over other amide compounds in hydrolytic stability. Because unlike the carbonamides, sulfonamides have remarkable resistance to acid and base hydrolysis.

In the literature, boiling in 60% H_2SO_4 for 3 h has been suggested for a complete hydrolysis of the sulfonamides.^[16] This provides regeneration of OMSA from its mercury compounds by treating with 6M HCl solutions without any hydrolysis.

More important is that its mercury compounds must also retain soluble in organic solvent to employ as mercury extracting agent. 2-ethyl hexanol has

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been proven to be suitable solvent. It dissolves not only OMSA but also its mercury compounds up to 1 mol L^{-1} concentrations and represents clear-cut phase separations in both cases. Another advantage of 2-ethyl hexanol is its nonvolatility which makes it useful for large-scale extractions.

As a result, these peculiarities have been combined in OMSA as a mercury specific extracting agent. Of course simplicity of its preparation is an additional advantage.

The mercury extraction from HgCl_2 solution can be depicted as follows:

Two mass balances can be written based on the residual Hg(II) and chloride concentrations which were determined analytically (0.11 mol L^{-1} and 0.468 mol L^{-1} , respectively). From those balances the following quantities can be calculated (see Appendix).

The distribution coefficient (ratio of mercury concentrations in organic and aqueous phases): $k_d = 1.273$.

Percentage mercury extraction (extraction coefficient), $G = 56.0\%$.

Percent of mercury extracted by formation of monoamido-mercury compound: 12.8% .

Percent of mercury extracted by formation of diamido-mercury compound: 43.2% .

Also we found that 99.2 of OMSA involved in mercury binding and the equilibrium constants are $K_1 = 36.07$ and $K_2 = 418.5$

Extractability of HgCl_2 is especially important, because chloride ions have a reasonable affinity toward mercuric ions and many anions accompanying with mercury are replaced by chloride ions. This affinity furnishes an analytical method for determination of chloride ions.^[17]

In other words a reagent capable of HgCl_2 extraction must also extract mercuric ions in greater extents in the presence of other common anions.

Indeed in nonbuffered conditions mercuric acetate and nitrate are removed in high percentages at the same extraction conditions (Table 1).

In those cases, the extraction coefficient rises up to 77.6% and 82.2% values for the nitrate and acetate salts, respectively. In the presence of those ions, extracted amounts are proportional to the HgCl_2 concentrations in water Fig. 1. As might be expected, the extraction curve for HgCl_2 substantially lies below the two curves. Nevertheless, over 0.2 mol L^{-1} mercury concentrations, in each case percentage extractions, retain higher than 50% .

High percentages of the mercury extractions for the nitrate and acetate salts indicate that mercury binding mostly occurs through formation of

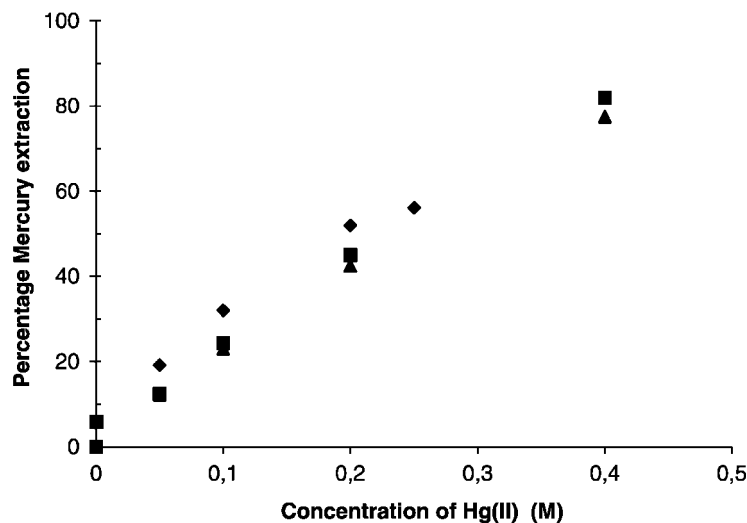


Figure 1. Concentration dependence of mercury extractions for acetate (■), nitrate (▲) and chloride (◆) salts (initial concentration of OMSA 0.4 M in $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}(\text{CH}_3\text{COO})_2$ extraction and 0.25 M in extraction of HgCl_2).

monoamido-mercury compounds. By assuming all the sulfonamides are consumed, it can be deduced that 55.2% of the sulfonamide is being consumed in monoamido-mercury formation in the extraction from HgNO_3 solution (0.4 mol L^{-1}). Similar estimation gives 64.4% for the extraction of mercuric acetate. The situation is reverse for the case of HgCl_2 extraction and only 12.8% of $\text{Hg}(\text{II})$ in monoamido form, as described above. Presumably the difference between the chloride and acetate or nitrate salts arises from kinetical factors. The first step of the reaction yielding monoamido-mercury compound is an interphase reaction and needs transport of mercury salt from aqueous phase to the organic phase. Transport of HgCl_2 must be slow in comparison to the other salts. Since the second step runs in the same phase this must be faster than the first step. Consequently ratio of the diamido compound becomes higher in the extraction of HgCl_2 .

Effect of Chloride Concentration

Extraction of HgCl_2 has been studied in the presence of NaCl in various concentrations, to inspect efficiency of the method for the extraction from sea water (average salt concentration of sea water is about 1 mol L^{-1}).

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Fortunately in up to 1.0 M NaCl concentrations the extracted amounts retain slightly higher than 50%. Apparently this result implies applicability of the method even in the presence of chloride ions (Fig. 2).

Interference of Foreign Ions

The interference of some foreign ions and selectivity of mercury extraction of the experiments have been repeated in competitive conditions, in the presence of FeCl_3 , ZnCl_2 , or CdCl_2 salts in 0.5 mol L^{-1} concentrations.

Analysis of the aqueous refined phase remaining from the extraction of mercury showed that (Table 2) the mercury concentration of the final aqueous solutions are almost the same with those for the case of HgCl_2 salt alone. Slight decrease in FeCl_3 and ZnCl_2 concentrations (3.6% and 2.6%, respectively) can be ascribed to the extraction by the organic solvent (2-ethyl hexanol) rather than extraction by OMSA. Concentrations of CdCl_2 and $\text{Pb}(\text{CH}_3\text{COO})_2$ in the aqueous phases are the same with those of the initial concentration higher than that of the mercury concentration. In lower concentrations the effect would be less than those values.

As a result, presence of the foreign ions studied does not affect extraction of HgCl_2 and $\text{Hg}(\text{CH}_3\text{COO})_2$ ions and only minute amounts of $\text{Fe}(\text{II})$ and $\text{Zn}(\text{II})$ are extracted simultaneously. These results reveal that OMSA is a specific extracting agent for $\text{Hg}(\text{II})$ salts.

Effect of the pH

Mercuric oxide precipitation occurs above pH:4.5. Due to this fact the pH effect was studied in pH:1–4 range. As it might be expected at lower pHs extracted mercury gradually reduces (Table 4). At pH:1.0 the extracted amount per mole of OMSA is still higher than 0.5 mole, which reveals that the extraction can be performed even in acidic region.

Stripping of the Extracted Mercury

Extracted mercury in the organic phase can be recovered by treating with H_2SO_4 or HCl solutions in various concentrations. Acid treatment is a reverse extraction process in which mercury is transferred from organic solvent to acid solution.

Table 4. pH-dependence of Hg(II) extraction from 25 ml 0.4 M Hg(CH₃COO)₂ solution.

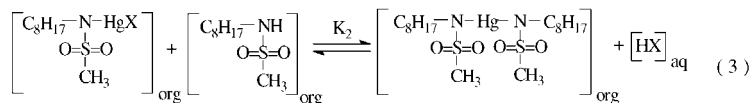
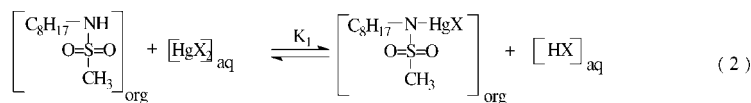
pH ^a	Final Hg(II) conc. (mol L ⁻¹)	Extracted mercury ^b (mol/mol OMSA)
1.00	0.152	0.620
2.10	0.087	0.783
3.10	0.078	0.805
4.05	0.070	0.825

^a Mercuric oxide precipitation occurs upon standing above pH:4.5

^b Mole per mol of OMSA (with 25 ml of 0.4 mol L⁻¹ OMSA solution in 2-ethylhexanol).

By acid treatment the equilibrium in Scheme 2 is simply shifted to the left. Possibility of the extraction even at pH:1 levels implies that the use of highly concentrated acid solutions is essential for splitting of the mercury. The acid concentration necessary can be estimated by using the equilibrium constants. Analysis of the acid solutions shows that 6 mol L⁻¹ HCl solution replaces 94% of extracted mercury in first contact. Whereas with 40% (v/v) H₂SO₄ (about 7.5 M) solution, 88.3 of mercury is recovered from the organic phase. This result seems to be rather confusing. Presumably in the former case chemical affinity of chloride ions to Hg(II) brings additional contribution for back-extraction of the mercury.

The remaining 6% mercury in organic phase can be washed out almost quantitatively when acid treatment is repeated using 25 ml of fresh acid



X: Cl⁻, CH₃COO⁻, NO₃⁻

Scheme 2.

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solution. The resulting mercury-free organic solution becomes regenerated by subsequent washing with water.

Due to ease of phase separation and hydrolytic stability of OMSA, we have observed that the extraction process can be repeated many times. In a separate experiment recyclability of the OMSA solution was tested by using mercuric chloride. In order to test the recycling ability of the OMSA solution, extraction and regeneration cycles of the organic phase were repeated 19 times without measuring mercury concentrations in the intermediate steps. The analysis was done at the last step and compared with the value in the initial step. Mercury loading capacity was found to be 3.48 mmol which is very close to the one 3.51 mmol in the first cycle.

In conclusion, the method presented seems to be promising and offers a simple approach for selective extraction of mercury ions.

- Solution of octyl methane sulfonamide is able to extract more than 56% of mercuric ions with different anions.
- Practically no interference comes from common foreign ions such as Fe(II), Zn(II), Cd(II), and Pb(II) ions.
- Presence of chloride ions reduces the extraction capacity. Nevertheless the extraction capacity, even in that case, is still satisfactory and the method is applicable up to 1 M NaCl concentrations.
- Due to hydrolytic stability of the sulfonamide linkage, N-octylmethane sulfonamide can be regenerated by highly concentrated acids and it can be recycled more than 20 times.
- Having these advantages, the present method seems to be promising and might be of interest to use in continuous extraction systems for large-scale mercury separations.

APPENDIX

The extraction, from aqueous HgCl_2 solution can be formulated using the following abbreviations.

- a: initial amide concentration (0.25 mol L^{-1})
- b: initial Hg(II) concentration. (0.25 mol L^{-1})
- x: concentration of monoamido-mercury compound in organic phase
- y: concentration of diamido-mercury compound in organic phase

In the experiments (performed in nonbuffered conditions) a and b were equal.

Since equal volumes (25 ml) of organic and aqueous solutions are used (0.25 mol L^{-1} of each) following stoichiometrical balances can be written in terms of molar concentrations of the species.

$x + y$: mercury in the organic phase

$a - (x + y)$: unreacted mercury in aqueous phase

$x + 2y$: concentration of the amide utilized in Hg bonding

$a - (x + 2y)$: unreacted amide concentration

The equilibrium constants:

$$K_1 = \frac{[\text{amide-HgX}]_{\text{org}}[\text{HX}]_{\text{aq}}}{[\text{amide}]_{\text{org}}[\text{HgX}_2]_{\text{aq}}}$$

$$K_2 = \frac{[\text{amide-Hg-amide}]_{\text{org}}[\text{HX}]_{\text{aq}}}{[\text{amide-HgX}]_{\text{org}}[\text{amide}]_{\text{org}}}$$

Determination of the free amide concentration in the extraction equilibrium is difficult. This was assigned indirectly by chloride analysis in the extraction of HgCl_2 .

Total chlorine after the extraction, coming from unreacted HgCl_2 and HCl.

$$0.468 \text{ M} = 2[a - (x + y)] + x + 2y = 2a - x$$

Since initial amide and Hg(II) concentrations are equal; $a = b = 0.25 \text{ mol L}^{-1}$. We have $x = 0.032 \text{ mol L}^{-1}$.

The unreacted mercury concentration (found); $0.110 \text{ M} = a - (x + y)$ and $y = 0.108 \text{ mol L}^{-1}$.

The unreacted amide concentration in organic phase;

$$a - (x + 2y) = 0.25 - (0.032 + 2 \times 0.108) = 0.002 \text{ mol L}^{-1}$$

The amide consumed for mercury extraction; $x + 2y = 0.248 \text{ mol L}^{-1}$.

Based on this rough estimation; we obtain, $x/a = 0.032/0.25 = 12.8\%$ of the initial mercury is in monoamido form.

And $y/a = 0.108/0.25 = 43.2\%$ in diamido form.

Totally $12.8\% + 43.2\% = 56.0\%$ of the mercury has been extracted.

And $0.248/0.25 = 99.2\%$ of sulfonamide is used in the extraction.

Since 1 mole proton released is accompanied by forming each mole of monoamido mercury and 2 moles for the diamido mercury compound, the HCl

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concentration should be

$$x + 2y = 0.032 + 2 \times 0.108 = 0.248 \text{ mol L}^{-1}$$

By using these values the equilibrium constants of the process in HgCl_2 extraction can be calculated. Since remaining amide concentration is very small and in the experimental error limits, it is difficult to find out exact values of the equilibrium constants based on these results. By substituting the above values we obtain approximate values of the constants as follows.

$$K_1 = \frac{x(x + 2y)}{[a - (x + 2y)][a - (x + y)]} = 36.07$$

$$K_2 = \frac{y(x + 2y)}{x[a - (x + 2y)]} = 418.5$$

These results reveal that most of the mercury has been extracted as diamido mercury and unreacted amide content is less than 1%. In other words almost all the sulfonamide groups are involved in mercury binding.

The distribution coefficient of Hg(II)

$$k_d = \frac{\text{mercury in organic phase}}{\text{mercury retaining in the raffinate}} = \frac{x + y}{a - (x + y)} = \frac{0.14}{0.11} = \mathbf{1.273}$$

Since volumes of aqueous and organic solution are equal to each other, the extraction coefficient, G for HgCl_2 should be:

$$G = \frac{\text{mercury concentration in extract phase}}{\text{initial mercury concentration}} = \frac{x + y}{a} = \frac{0.25 - 0.11}{0.25} = \mathbf{0.56}$$

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