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Thermodynamics of Extraction of Selenium by Tri-iso-octyl Amine (TIOA) from Chloride Medium

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ABSTRACT

The equilibrium distribution of selenium in hydrochloric acid medium and with the chloride salt of tri-iso-octylamine (TIOA) in xylene was studied. Experimental data were analyzed graphically and numerically to determine the stoichiometry of the extraction species. It was found that the extraction reaction is endothermic ($\Delta H = +17.060\,\mathrm{KJ/mol}$). Selenium was extracted by the reaction:

$$2[R_3N^+HCl^-]_{org} + [SeCl_6^{2-}]_{aq} = [(R_3N^+H)_2\ SeCl_6^{2-}]_{org} + 2[Cl^-]_{aq} \qquad (1)$$

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The effect of extractant concentration, equilibration period, diluents, and diverse ion and stripping agents on the extraction of selenium were studied. The distribution constant and the thermodynamic parameters enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) were evaluated.

Key Words: Selenium; Extraction; TIOA; Thermodynamic parameters; Xylene.

INTRODUCTION

Selenium exhibits both photovoltaic actions (where light is converted directly into electricity) and photoconductive action (where the electrical resistance decreases with increased illumination). These properties make selenium useful in the production of photocells and exposure meters for photographic use, as well as solar cells. Selenium is also able to convert AC electricity to DC, and is extensively used in rectifiers. The solid selenium is a p-type semiconductor and is useful in electronic and solid-state applications. Selenium is used in photocopying for reproducing and copying documents and letters. It is used by the glass industry to decolorize glass and to make ruby-colored glasses and enamels. Selenium is presently the primary wastewater treatment challenge for many petroleum refineries. It is also present in significant quantities in wastewaters from coal-fired power plants. A suspected carcinogen, selenium is also harmful to fish and fowl when present in surface waters.

Selenium is widely distributed in various environmental samples in trace amounts. It is classified as both an essential micronutrient for many animals as well as toxic at elevated levels. It can be considered either as an impurity in a number of processes or as a toxic element that needs to be eliminated.

The development of a procedure for the determination of selenium in serum using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) was described. The method eliminates the need for a lengthy sample digestion procedure (a requirement with many methods for the analysis of biological samples), utilizing a simple $1 + 19$ dilution of the serum with 1% nitric acid. Many of the interferences normally associated with the determination of selenium by inductively coupled plasma mass spectrometry (ICP-MS) are successfully eliminated with careful optimization of the ETV temperature program and modifier system.[1]

Selenium was determined by flow injection analysis based on the selenium (IV)-catalyzed reduction of 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2*H* tetrazolium bromide.[2] Separation of selenium from anode slime using tri-*n* butyl-1-phosphate as a extractant was investigated.[3] Elimination of selenium in effluent from precious metal refinery was studied.[4] The stability of selenium species in water and urine as well as in extracts of fish and soil certified reference materials was investigated. Speciation analysis was performed by on-line coupling of anion exchange high-performance liquid chromatography (HPLC) with ICP-MS.[5]

An analytical method for the speciation of selenomethionine, selenocystine, selenite, and selenate by HPLC with atomic spectrometric detection was presented. An organic polymeric, strong anion exchange column was used as the stationary phase in combination with an aqueous solution of 6 mmol/L salicylate ion at pH 8.5 as the mobile phase, which allowed the isocratic separation of the four selenium analyses within 8 min. The separated selenium species were detected on-line by flame atomic absorption spectrometry (FAAS) or ICP-MS.[6] Extraction reagents for selenium have been based on ketone and aldehyde[7–11] and only recently, the use of amines for the extraction of selenium was considered.

The conventional pyrometallurgical method of separation of selenium requires high energy consumption and gives low-extraction efficiency. The selenium is recovered mainly from anode slime obtained during electrorefining of copper by alkali fusion technique.[12] Separation of this element from complex sulfide matrix is difficult. With this aim, the simple method has been developed for extraction of selenium with tri-iso-octylamine (TIOA). The present investigation envisages the development of an energy efficient technique for recovery of selenium from aqueous solution.

The extraction of metals such as chromium from various acidic media using high-molecular-weight TIOA has been reported.[13–15] But there are no data available on the use of the tertiary amine TIOA for the extraction of selenium, thus in the present work, the concentration dependency of the equilibrium distribution of the selenium between hydrochloric acid solutions and the chloride salt of the tertiary amine TIOA in xylene was studied.

EXPERIMENTAL

Reagents

The TIOA, donated by Henkel Corporation, USA, was used. The extractant was used without any further purification. Standard stock solutions of selenium were prepared by dissolving 2.21 g of sodium selenite (Na_2SeO_3) (BDH Chemicals Ltd., Poole, England) in 1 M hydrochloric acid and diluted to 1000 mL with double distilled water.[16] All organic and inorganic reagents used in this study were of analytical grade.

Procedures

The organic phase was prepared by diluting a measured volume of the amine with reagent grade *o*-xylene. Extractions were carried out by the following procedure: equal volumes of aqueous and organic phases of known concentrations were placed in a (1 L) five-neck, flat bottom flask using a mechanical stirrer at 1000 ± 10 rpm. The flask was immersed in a water bath controlled by a Beckmann thermometer to maintain uniform temperature ($\pm 1^\circ$C). After separating the phases, the selenium in the aqueous phase was determined by a Perkin Elmer FAAS (model 2380) equipped with a Perkin Elmer hydride generating system (Model MHS-10) and a deuterium background corrector was used to record the absorption signals of all measurements. Peak area values were considered for signal processing. An electrodeless discharge lamp (EDL) of selenium was used with a wavelength setting of 196 nm. The selenium concentration in the organic phase was calculated from the difference between the selenium concentration in the aqueous phase before and after the extraction. All the instruments used in the investigation were calibrated using standard quality assurances practices. The relative standard deviations of the experimental results are kept within 1.5%.

RESULTS AND DISCUSSION

Effect of Temperature

The effect of temperature on the extraction of selenium from aqueous phase of $0.127\,\text{mmol/dm}^3$ selenium in 6 mol/L HCl by the chloride salt of TIOA in xylene was studied. The results show that there was an increase in selenium extraction as the temperature increased.

The change of the distribution constant (K_D) with temperature is expressed by the van't Hoff equation

$$\frac{d(\log K_D)}{d(1/T)} = \frac{-\Delta H}{2.303R} \tag{2}$$

The plot of $\log K_D$ vs. $1/T$ (Fig. 1) is linear with a slope of -0.891. The enthalpy change of the extraction reaction carried out at constant pH 0.70 was evaluated as $\Delta H = +17.060\,\text{kJ/mol}$, which means it is an endothermic reaction. The positive enthalpy value indicates that the extraction of selenium with TIOA in xylene is favorable with a rise in temperature (Table 1).

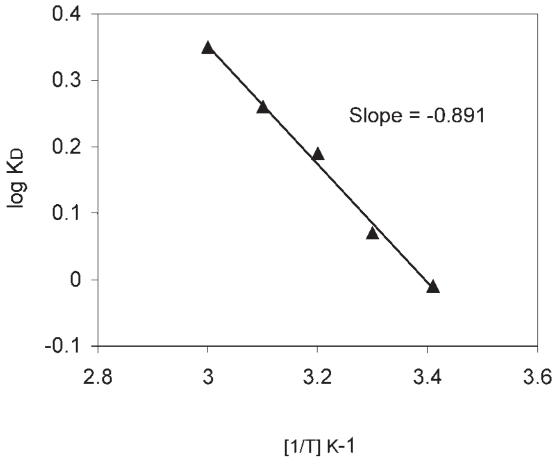

Figure 1. Plot of $\log K_D$ vs. $1/T$ per K. Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

The free energy change (ΔG) and entropy (ΔS) were calculated from Eqs. (3) and (4).

$$\Delta G = -2.303RT \log K_D \tag{3}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{4}$$

The negative values of free energy implies that the extraction reaction is spontaneous.

Table 1. Effect of temperature on extraction of selenium.

Temperature (K)	$\log K_D$	ΔG (kJ/mol)	ΔS (J/K/mol)
303	0.07	−0.406	0.061
313	0.19	−1.139	0.059
323	0.26	−1.608	0.057
333	0.35	−2.233	0.062

Note: Initial metal concentration 0.127 mmol/dm^3 selenium in 6 mol/L HCl. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

Influence of the Initial Concentration of the Extractant

The influence of the variation of the extractant (TIOA) concentration on the extraction of selenium was studied. Figure 2 shows an increase in selenium extraction as the extractant concentration is increased. The results indicated that the optimum concentration of TIOA was 44.5×10^{-3} mol/L for nearly complete extraction of selenium by a single-stage operation.

From the experiment, it was observed also that two amine ligands react with one Se(IV) ion. This was determined by the plot of $\log K_D$ vs. $\log[R_3N^+HCl^-]$ with a slope 1.97, which is close to 2 (Fig. 3), from the following equations:

$$[SeCl_6^{2-}]_{aq} + n[R_3N^+HCl^-]_{org} = [(R_3N^+H)nSeCl_6^{2-}]_{org} + n[Cl^-]_{aq} \tag{5}$$

$$\text{Extraction equilibrium } (K_{ex}) = \frac{[(R_3N^+H)nSeCl_6^{2-}]_{org}[Cl^-]^n_{aq}}{[SeCl_6^{2-}]_{aq}[R_3N^+HCl^-]^n_{org}} \tag{6}$$

$$\text{Distribution constant } (K_D) = \frac{[(R_3N^+H)nSeCl_6^{2-}]_{org}}{[SeCl_6^{2-}]_{aq}} \tag{7}$$

therefore;

$$K_{ex} = \frac{K_D[Cl^-]^n_{aq}}{[R_3N^+HCl^-]^n_{org}} \tag{8}$$

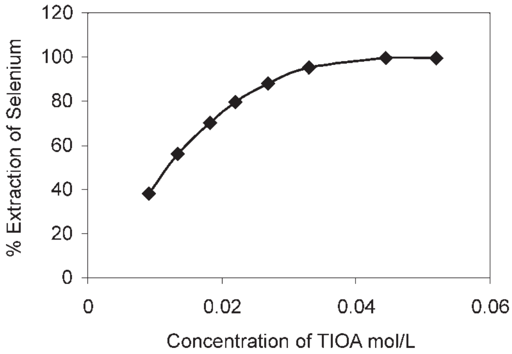

Figure 2. Plot of percentage extraction vs. [TIOA] mol/L. Initial metal concentration 0.127 mmol/dm^3 selenium. O/A ratio 1.

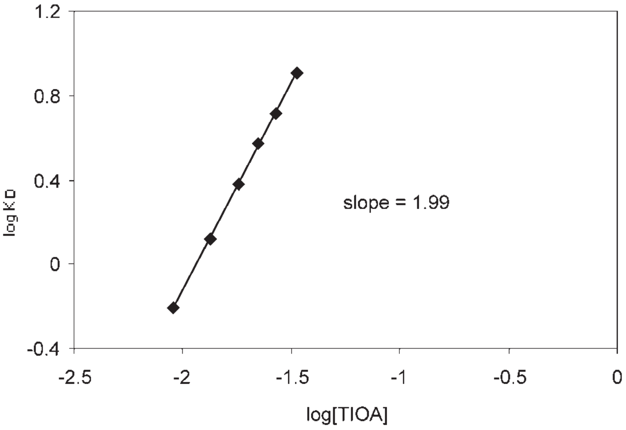

Figure 3. Plot of log K_D vs. log[TIOA]. Initial metal concentration 0.127 mmol/dm^3 selenium. O/A ratio 1.

For constant [Cl]

$$\log K_D = n \log[R_3N^+HCl^-]_{org} + \text{constant} \tag{9}$$

Effect of Contact Time

Experiments on the influence of contact time on the extraction were carried out by shaking the aqueous solution of 0.127 mmol/dm^3 selenium and an organic solution of 44.5×10^{-3} mol/L of TIOA in xylene at O/A ratio of 1 at 30°C, for various lengths of time. It was observed that selenium was completely extracted in 90 sec of shaking time. A clear phase separation within 2 min was also observed (Fig. 4). A shaking time of 2 min was taken for the extraction of selenium in all the experiments, that followed.

Effect of Acid and Chloride Salt

The extractions were carried out at 30°C, varying the selenium ion concentration in aqueous phase and using various concentrations of HCl. Figure 5 shows that the distribution constant of selenium reaches a maximum at high acid concentrations. There is a difference in the behavior of this extraction system with the selenium used; for each HCl acid concentration, the distribution constant (K_D) increases as the initial concentration of selenium is

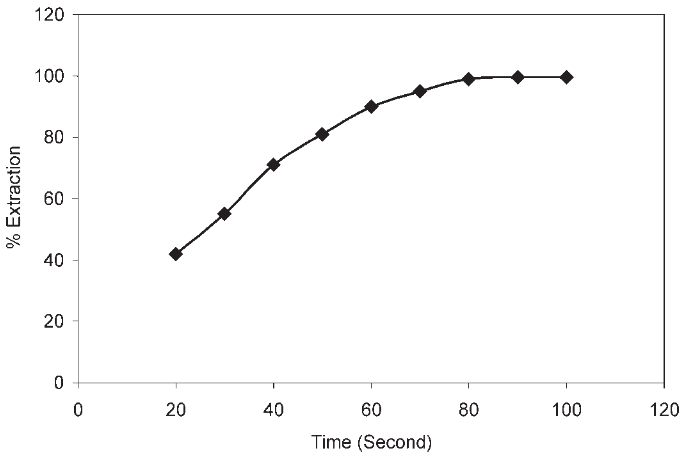

Figure 4. Plot of percentage extraction vs. time (sec). Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5 × 10^{-3} mol/L TIOA in xylene. O/A ratio 1.

decreased (Fig. 6). This behavior may be explained from the following set of equations

$$SeCl_6^{-2} + [2(R_3N^+HCl^-)]_{org} = [(R_3N^+H)_2SeCl_6^{-2}]_{org} + 2Cl^- \qquad (10)$$

To achieve this exchange, the amine is first converted to the appropriate amine salt to provide an anion to exchange with the metal species

$$[R_3N]_{org} + HCl = [R_3N^+HCl^-]_{org} \qquad (11)$$

This shows the acidification of amine extractants to form an amine salt or ion pair $[R_3N^+HCl^-]$ in the organic phase. Therefore, the extraction of selenium from chloride system undergoes an ion–association mechanism.

It was investigated that in the ion–association extraction system, high concentrations of electrolyte, like $MgCl_2$ and $ZnCl_2$, are effective in increasing the extent of extraction. The addition of such salts, referred to as salting-out reagents, serves two purposes. The first and more obvious is to aid the direct formation of the complex by the mass action effect due to the formation of a chloro complex. It is promoted by increasing the concentration of chloride ion. Secondly, as the salt concentration increases, the concentration of free water decreases because the ions require a certain amount of water for hydration. This decreases the solubility of complex $[(R_3\ N^+H)_2\ SeCl_6^{-2}]$ in aqueous phase.

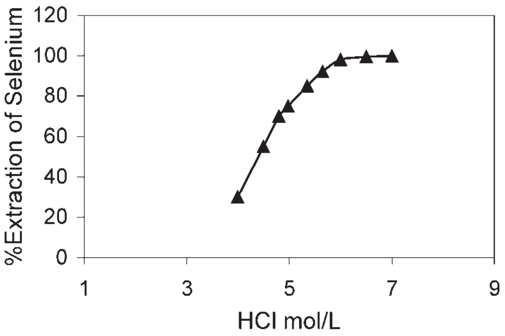

Figure 5. Plot of percentage extraction vs. HCl mol/L. Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

Effect of Carbon Chain of Amine Extractant

One important factor influencing metal extraction by amine is the nature of the carbon chain. Another factor is the number of carbon atoms in the chain. Experiments were conducted with a number of tertiary amines, where carbon chain length was varied. For all the amines of 44.5×10^{-3} mol/L solution was prepared with xylene as solvent. The result, shown in Table 2 indicates

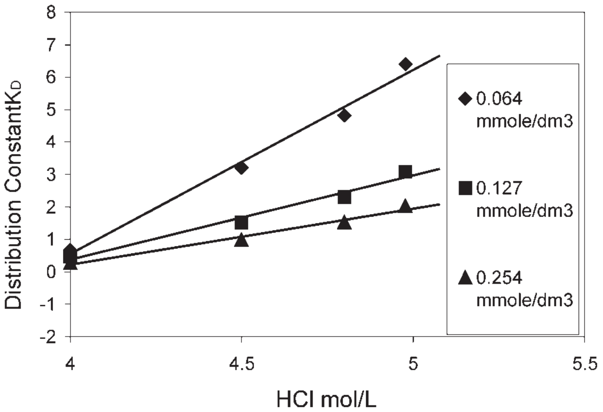

Figure 6. Plot of distribution constants (K_D) vs. HCl mol/L. Initial metal concentration of selenium 0.064, 0.127, and 0.254 mmol/dm^3. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

Table 2. Effect of carbon chain of amine extractant on the extraction of selenium.

Tertiary amine	Percentage extraction of selenium
Tributylamine	65.5
Trihexlamine	88.5
Methyl di-*n*-octylamine	96.5
Tricaprylamine	98.5
Tri-iso-octylamine	99.5
Trilaurylamine	99.0

Note: Initial metal concentration 0.127 mmol/dm^3 selenium in 6 mol/L HCl. Organic phase: 44.5×10^{-3} mol/L of various tertiary amines in xylene. O/A ratio 1.

a sharp increase in extraction with the increase of carbon chain length. Extraction of selenium remained constant with amines having carbon chain lengths from C_8 to C_{12}. From Table 2, it is also observed that with TIOA and trilaurylamine, the extraction of selenium was quantitative. Although, extraction was almost quantitative with tricaprylamine, phase separation was not clear, as observed with TIOA.

Effect of Acids on Extraction

The effect of sulfuric, nitric, and perchloric acids on the extraction of selenium were investigated. The results are shown in the Table 3, which shows that sulfuric acid above 2 M reduced the extraction. Nitric and perchloric acids interfered even at the concentration of 0.01 mol/L. This is due to the salt effect of various ions. Salt effects generally decrease the metal extraction by amine in the order $ClO_4^- > NO_3^- > SO_4^-$.

Effect of Diluents

The extraction of selenium was carried out with 44.5×10^{-3} mol/L of TIOA in different diluents. The results are given in Table 4. From the results, it is clear that effective extraction occurred in xylene followed by methyl isobutyl ketone. Though, extraction was effective in methyl isobutyl ketone, clear phase separation was much slower compared to xylene. Moreover, the solubility of methyl iso-butyl-ketone increases with an increase in acidity. Among all the diluents used, xylene was found to be the most suitable diluent for

Table 3. Effect of acids on extraction of selenium.

Acids	Concentration (mol/L)	Percentage extraction
H_2SO_4	0.5	99.5
	1.0	99.0
	2.0	98.2
	3.0	95
HNO_3	0.01	92
	0.02	85.5
	0.05	74.5
	2.5	52.5
$HClO_4$	0.01	90.0
	0.02	75.5
	0.05	43.0
	0.10	25.5

Note: Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

the extraction of selenium. It is so, because better extraction and clear phase separation took place in xylene within 2 min.

Effect of Stripping Agents

Selenium extracted into organic phase (TIOA in xylene) was stripped with different strengths of stripping agents. A reduction of absorption signal

Table 4. Effect of solvent on the extraction of selenium.

Solvents	Percentage extraction of selenium
Kerosene	80.5
Toluene	70.5
Xylene	99.5
Carbontetrachloride	86.0
Chloroform	35.0
Methyl isobutylkotone	98.5

Note: Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

was observed for nitric acid as a stripping agent with a concentration range of 0.5–1.0 mol/L. It was observed also that in increasing the nitric acid concentration, the stripping of selenium was decreased. Similar suppression of absorption signals were also observed for sulfuric acid, but this was less pronounced than for nitric acid.

The organic phase was vigorously shaken with different concentrations of hydrochloric acid (0.05–2.0 mol/L) and then left for clear phase separation. The results indicated that the recovery of selenium was effective while shaking the organic phase with 0.08-M solution (Fig. 7). For all experiments, a 0.1-M HCl solution was used as stripping agent. The optimum contact time for stripping was 2 min.

Effect of Diverse Ions

The effect of diverse ions on the recovery of 1000 μg selenium was investigated by adding 100- to 500-fold known amounts of each ionic species to be examined. The amount of each ionic species added to investigate the effect of interfering foreign ions is presented in Table 5. The error of recovery of selenium in presence of following ions was not more than ± 1.5%.

CONCLUSION

From the results, it is observed that selenium is extracted with TIOA in xylene as a moderator by an ion–association mechanism. The extracted species in the organic phase is $[(R_3N^+H)_2SeCl_6^{-2}]$. The thermodynamic

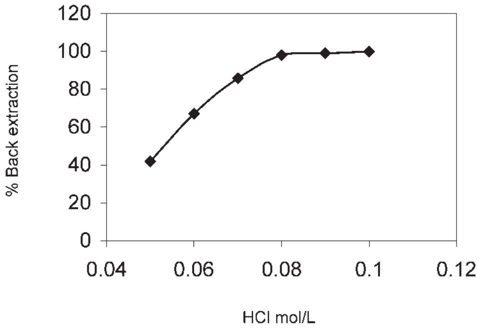

Figure 7. Plot of percentage back extraction vs. HCl mol/L. Initial metal concentration 0.127 mmol/dm^3 selenium. O/A ratio 1.

Table 5. Effect of diverse ions on extraction of selenium.

Ions	Added as	Taken (μg)
K^+	KCl	1,000
Na^+	$NaCl$	1,000
Mg^{2+}	$MgCl_2$	1,000
Ca^{2+}	$CaCl_2 \cdot 2H_2O$	1,000
Ba^{2+}	$BaCl_2 \cdot 2H_2O$	1,000
Sr^{2+}	$SrCl_2 \cdot 2H_2O$	1,000
Co^{2+}	$CoCl_2$	1,000
Mn^{2+}	$MnCl_2 \cdot 4H_2O$	1,000
Ni^{2+}	$NiCl_2 \cdot 6H_2O$	1,000
Zn^{2+}	$ZnSO_4 \cdot 7H_2O$	1,000
Cu^{2+}	$CuSO_4 \cdot 5H_2O$	1,000
Cd^{2+}	$CdCl_2$	500
Al^{3+}	$AlCl_3$	2,000
Cr^{3+}	$CrCl_3$	500
Hg^{2+}	$HgCl_2$	200
As^{3+}	$NaAsO_2$	400
Sb^{3+}	$NaSbO_2$	400
Sn^{2+}	$SnCl_2 \cdot 2H_2O$	500
Pd^{2+}	$PbCl_2 \cdot 2H_2O$	500
Zr^{4+}	$ZrOCl_2 \cdot 8H_2O$	500
Ti^{4+}	$TiCl_4 \cdot 4H_2O$	500
Fe^{3+}	$FeCl_3 \cdot 6H_2O$	2,000

Note: Initial metal concentration 0.127 mmol/dm^3 selenium. Organic phase: 44.5×10^{-3} mol/L TIOA in xylene. O/A ratio 1.

functions enthalpy (ΔH), entropy (ΔS), and free energy changes (ΔG) in the extraction of selenium with TIOA were evaluated. The extraction reaction is an endothermic process with the extraction percentage increasing with the increasing temperature. Another important feature of the proposed method is that extraction of selenium using 44.5×10^{-3} mol/L TIOA in xylene from aqueous solution resulted in 99% recovery within 2 min.

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