Asian Journal of Chemistry Vol. 3, No. 3 (1991) 317–323

SOLVENT EXTRACTION OF PALLADIUM WITH 8-MERCAPTOQUINOLINE †

(Late) ARVIND T. RANE and DEEPAWATI R. NEPALI*
Tata Institute of Fundamental Research
Bombay 400 005, India.

The solvent extraction equilibrium and kinetics of palladium extraction by 8-mercaptoquinoline have been studied radiometrically in chloroform, at ambient temperature (28°C), and ionic strength 0.1M. The extractable complex is a diadduct, *i.e.* two molecules of the reagent are coordinated to the palladium(II) chelate. The adduct formation constant in chloroform and the overall formation constant of the palladium chelate in aqueous solution have been determined. The palladium complex is extractable from pH 1 to 9 uniformly. The rate of palladium(II) extraction by 8-mercaptoqunoline is first order with respect to [8-mercaptoquinoline] and the extraction rate constants were evaluated. Procedure was developed for the radiochemical separation of high specific active ^{100}Pd from cyclotron irradiated ruthenium.

INTRODUCTION

8-Mercaptoquinoline or thiooxine, the S-analogue of 8-quinolinol is a very useful analytical reagent. Unlike 8-quinolinol, it is capable of removing metal ions from strongly acidic solutions[1]. Kealy and Freiser[2] have shown the effect of introduction of substituent into the molecule of an organic chelating agent, resulting in changes in its chelating ability in additon to the effects on chemical and physical properties. They investigated the molecular structural influences on equilibrium aspects of 8-mercaptoquinoline and its 2-methyl analogue. The also studied qualitative reactions of 25 metal ions with 2-methyl-8-mercaptoquinoline and confirmed the decrease in stability arising from the introduction of 2-methyl group in 8-mercaptoquinoline indicating the steric influence of the methyl group in the hydrated 1:1 metal complexes. Haraguchi and Freiser[3] studied the kinetics and mechanism of solvent extraction of nickel(II) with 8-mercaptoquinoline in chloroform in the pH range of 5.9–6.8 at ambient temperature using a high speed stirring apparatus. Rane and Nepali[4] determined the equilibrium distribution coefficients and adduct formation constants for the extraction of cobalt(II) with 8-mercaptoquinoline along with the formation constants of the nitrogen base adducts. An attempt is made here to study the solvent extraction equilibrium and kinetics of palladium(II) with 8-mercaptoquinoline and its radiochemical separation from ruthenium.

---

† This paper was presented at the 10th Symposium on Radiochemistry and Radiation Chemistry held at Nagpur, India February, 1990.

EXPERIMENTAL

A kahn type shaking machine fitted with a wooden box, in which stoppered centrifuge tubes (10 cm^3) could be accommodated, was used to equilibrate solutions at ambient temperature. Radioactivity was counted on a NaI(Tl) detector connected to a scintillation spectrometer supplied by ECIL (India).

8-Mercaptoquinoline or thiooxine was obtained from Fluka, Ag, as the hydrochloride ($C_9H_7NS.HCl$). Stock solution of thiooxine was prepared by dissolving the reagent in 3M hydrochloric acid. The chloroform solution of the reagent was prepared just before the extraction study by extracting the reagent from the aqueous phase at pH 5.0 from an acetate buffer solution. The concentration of the reagent could be checked by measuring the absorbance at 325 nm[5].

High specific active palladium-109 ($t_{1/2}$ = 13.4 h) was obtained by irradiating 2 mg of $PdCl_2$ in CIRUS, BARC, Trombay. $PdCl_2$ after dissolution in conc. HCl, was sufficiently diluted by distilled water. Aliquots of 0.1 ml ^{109}Pd stock solution were taken for the distribution study. A set of Clark and Lubs buffer solutions were prepared from 1 to 9 pH varying successively by 0.2 units. The ionic strength was maintained constant at 0.1M by adding requisite amounts of sodium perchlorate to the buffers.

Procedure

The extraction of palladium was studied by equlilibrating 5ml of ^{109}Pd buffered solution, at constant ionic strength (μ = 0.1M) and 5 ml of thiooxine solutions in chloroform of varying concentrations ($1.5 \times 10^{-4} - 6.7 \times 10^{-5}$M) at various pH, 1–9, by shaking for 45 min. at ambient temperature (28°). The mixtures were centrifuged after equilibration and equal volumes were pipetted and counted separately at constant geometry. For the extraction kinetic study, samples were equilibrated for varying time intervals.

RESULTS AND DISCUSSION

Preliminary experiments were done by using ^{103}Pd($t_{1/2}$ = 17 d) for extractions. Due to very low specific activity of ^{103}Pd, log *D* value were obtained. Hence further work was carried out using high specific active ^{109}Pd($t_{1/2}$ = 13.4 h). The extraction of a chelate is illustrated by a plot of log *D* vs pH, at a constant [reagent] in the organic phase. This plot gives curves parallel to each other and to *x*-axis at different [reagent]. Normally in such plots, log *D* increases initially in the lower pH region and then eventually reaches to a constant log *D*, the distribution coefficient of the chelate, K_{DC}. In the case of palladium, this does not arise as palladium is extracted even in the acidic medium, i.e. very low pH region. Beyond pH 6.0, however, there is some depression in the extraction curve (Fig. 1). This may be due to the fact that palladium has tendency to get back extracted at higher pH. The tendency of the extraction curves, running parallel to each other along with the *x*-axis and shifting curves to higher log *D* values with the increase in [reagent], indicates the formation of a self-adduct. Similar behaviour *i.e.* extraction at very low pH and extraction curves running parallel to each other was observed in the extraction of indium(III) with thiooxine[6].

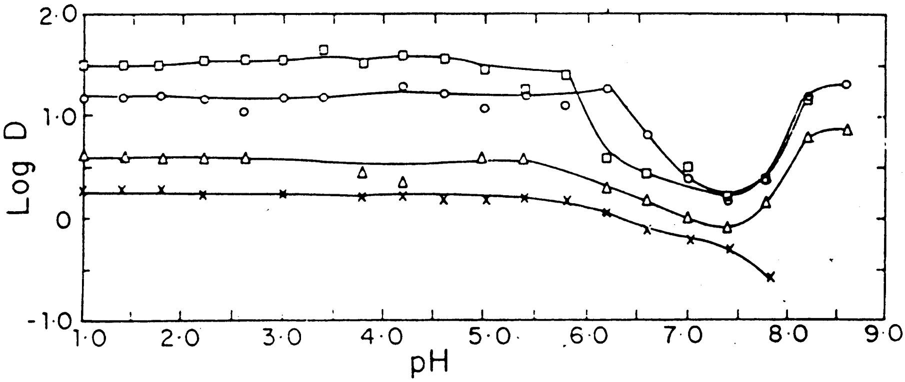

Fig. 1. Plots of log D vs pH. Extraction of Pd(II) with 8-mercaptoquinoline at different concentrations of the reagent at various pH.x6.68×10^{-5}; Δ8.49×10^{-5}; O 1.05×10^{-4}; □ 1.48×10^{-4} [8-*MQ*]

The total number of thiooxine molecules involved in the formation of Pd(II)-8-mercaptoquiolinate adduct could be determined from the slope of the plot of log *D* vs log [8-*MQ*]. This plot consists of two linear portions

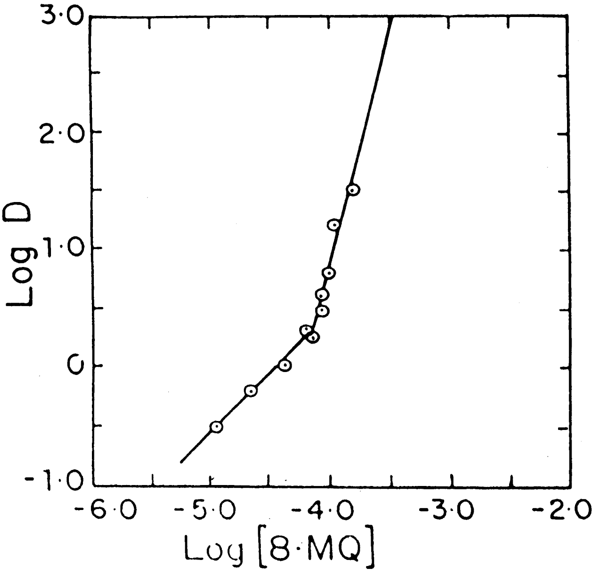

Fig. 2 Plot of log *D* vs log [8-*MQ*] pH = 1.0 Slope = 4.0

for [8-MQ] → 0, $\log D = \log K_{ex} + 2 \log [8\text{-}MQ]_0 + 2\,\mathrm{pH}$ (1)

for [8-MQ] → ∞, $\log D = \log k_{ex} + \log K_{AD} + 2\,\mathrm{pH} + (2 + a) \log [8\text{-}MQ)_0$ (2)

Such plot was obtained by extracting palladium with 8-MQ of various concentrations between 1.05×10^{-5} and 1.5×10^{-4} M at pH 1.0. The slope of this plot at lower $[8\text{-}MQ]_0$ is slightly less than two and suddenly increases to four at higher $[8\text{-}MQ]_0$ (Fig. 2). The intersection of these two linear curves gives the value of the adduct formation constant K_{AD} in chloroform[7]. The slope four of this plot indicates that two additional reagent molecules are involved in the formation of a diadduct having an empirical formula, $PdQ_2.2(8\text{-}MQ)$. From the intercept of this plot, the extraction constant, K_{ex} could be evaluated from the equation (2).

The overall formation constant of the palladium chelate in the aqueous phase could be calculated from the plot of log D-2 *log [8-MQ]*$_0$ vs PQ^- is the negative logarithm of the anion concentration of 8-MQ in the aqueous phase, which takes into account the variations in pH and the [reagent], simultaneously, giving two intersecting plots. Q^- could be calculated from the pK and K_D values of the reagent. The K_f value may be obtained from the intersection of the linear curves i.e. $pQ^- = 1/2\,K_f$ (Fig. 3). The overall formation constant could also be calculated from the intercept of this plot by proper substitution. The plot of log D-2 log $[HQ]_0$ vs pQ^- gives an intercept $\log (K_1K_2K'_{DC}K_{AD})/K_D$, where K'_{DC} is the distribution coefficient of the adduct

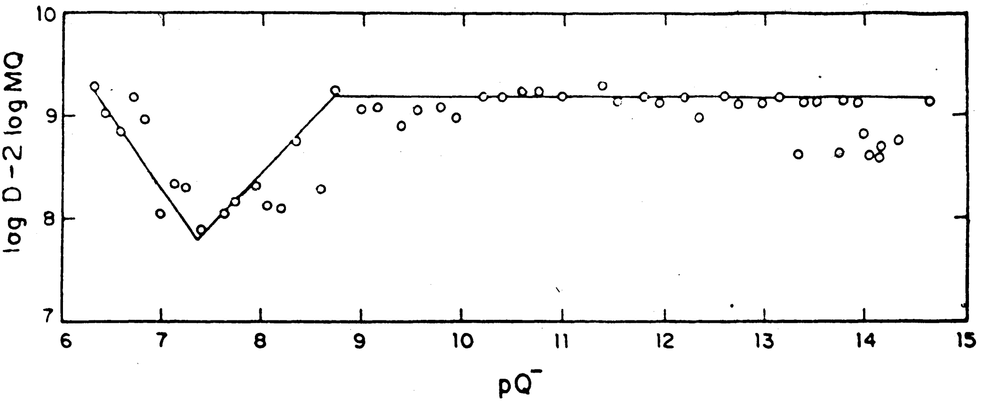

Fig. 3 Plot of log D − 2 log [8-MQ] vs pQ^-

$$K'_{DC} = \frac{[PdQ_2 \cdot 2(8 - MQ)]_0}{[PdQ_2 \cdot 2(8 - MQ)]}$$

$\log K'_{DC}$ is $\log D_{max}$ obtained in the plot of log D-2 log [8-MQ] vs $pQ^- = K_D$ in the distribution coefficient of the reagent and K_1 K_2 in the overall formation constant, K_f. The value[3] of $\log K_D$ was taken as 2.57. The values of the constant are given in Table 1.

TABLE 1
EQUILIBRIUM CONSTANTS FOR PALLADIUM(II) CHELATES OF 8-SMERCAPTOQUINOLINE

$\log K_{ex}$	$\log K_{AD}$	$\log K_f$
10.74	4.13	17.2

Extraction Kinetics

The kinetics of extraction of Pd(II) was studied by equilibrating ^{109}Pd buffered solution at pH 1.0 (μ = 0.1M) with thiooxine solution in chloroform of different concentrations between $6 \times 10^{-5} - 1.2 \times 10^{-4}$ M, at ambient temperature (28°). The solutions were equilibrated by shaking the mixtures for different time intervals. The aqueous phases of the samples were counted after centrifugation. The rate of Pd removed from the aqueous phase is

$$\frac{d}{dt}(\mathrm{Pd}^{2+}) = k(\mathrm{Pd}^{2+})(Q^{2-}) \qquad (3)$$

where k is forward reaction rate constant. Then the rate constant for the forward extraction reaction is given as[9].

$$k_t = \frac{A^0 - A_e}{A^0} \ln \frac{A^0 - A_e}{A^0} \qquad (4)$$

where A_0, A_e and A_t are the palladium counting rates at the start, equilibrium and at time t, respectively, in the aqueous phase.

The kinetic data obtained for the extraction of Pd(II) with thiooxine have been plotted as per equation (4) for different [8-MQ] when straight line plots were

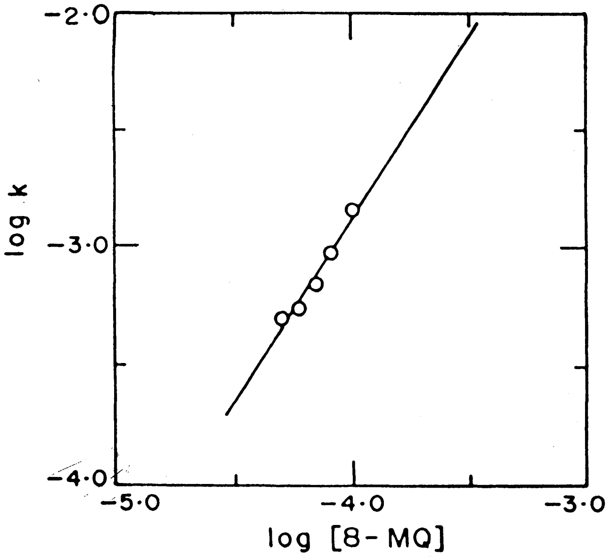

Fig. 4 Dependence of the observed rate constant, k, as a function of [reagent].

obtained with varying slopes. The straight line plots confirm that the rate of extraction is first order w.r.t. Pd(II). The slope of these plots give directly the value of appropriate rate constants for the extraction of Pd(II). These are given in Table 2. Linearity of the plot of log *K* vs log [8-*MQ*] showed the dependence of the observed rate constant as a function of [reagent] (Fig. 4).

TABLE 2
EXTRACTION RATE CONSTANTS OF PD(II)BY
8-MERCAPTOQUINOLINE AT 28°C pH = 1.0

[8-MQ]×10^5 mol.$^{-1}$	k×10^4(sec^{-1})
5	5.9
6	5.49
7	6.8
8	9.45
10	14.14

Separation of ^{100}Pd from ruthenium

The advantage of the extraction data obtained in the present study was taken in the radiochemical separation of ^{100}Pd from ruthenium. Specpure ruthenium metal was bombarded with particles in the Variable Energy Cyclotron, B.A.R.C., Bombay. ^{100}Pd$_{(t1/2 = 3.7d)}$ was produced by the following reaction

$$\text{Ru } (\alpha, xn) \text{ Pd}$$

where x is the number of neutrons released depending upon the mass number of Ru. The Ru target, after irradiaton, was fused with sodium peroxide in a platinum crucible. The fused mass was dissolved in distilled water and made acidic, with hydrochloric acid. 0.2 mg of Pd carrier were added to the solution and ^{100}Pd was extracted with thiooxine solution in chloroform (~ 10^{-2} M). The organic phase was washed thoroughly with distilled water. ^{100}Pd was back extracted with dil. ammonia solution. High specific active ^{100}Pd was obtained after removal of ammonia by evaporation, free from ruthenium contamination. The radiochemical purity of ^{100}Pd was checked by taking its γ-ray spectrum.

REFERENCES

1. Yu. A. Bankovskii, Chelate Chemistry of 8-Mercaptoquinoline and Its Derivatives, Izdatelstvo Zinatne, Riga, USSR (1978).
2. D. Kealy and H. Freiser, *Anal. Chem.*, **38,** 1577 (1966).
3. KI Haraguchi and H. Freiser, *Anal. Chem.*, **55,** 656 (1983).
4. A.T. Rane and D.R. Nepali, *J. Radional. Nucl. Chem.*, **90,** 39 (1985).
5. Yu. A. Bankovskii, L.M. Chera, andA.F. Ievin'sh, *Zh. Anal. Khim.*, **18,** 668 (1963).

6. A.T. Rane and D.R. Nepali, *Indian J. Chem.*, **25A,** 846 (1986).
7. K.S. Bhatki, A.T. Rane, H. Freiser, *Indian J. Chem.*, **15A,** 983 (1977).
8. F.C. Chou, Q. Fernando and H. Freiser, *Anal. Chem.*, **37,** 361 (1965).
9. D.S. Flett, D.N. Okuhara and D.R. Spink, *J. Inorg. Nucl. Chem.*, **35,** 2471 (1973).

(Invited contribution: 13 June 1990) AJC–192