# Solvent extraction equilibria of palladium(II) complex with 5,8-diethyl-7-hydroxydodecan-6-one oxime in some organic diluents

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Received 13 June 1991; revised 3 October 1991; accepted 22 November 1991

The extraction equilibrium behaviour of palladium(II) from aqueous chloride solution with 5,8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63) in seven organic solvents has been studied. The overall extraction equilibrium is represented by the expression:

$$Pd^2 + 2\,HL_{(0)} \overset{K_{ex}}{\rightleftharpoons} PdL_{2(0)} + 2H^-$$
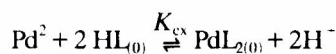
The distribution constant (K_{DR}) of LIX 63, determined between the organic solvents and water, increases in the order: n-heptane < n-hexane < carbon tetrachloride < benzene < dichloromethane < toluene < chloroform. The extraction equilibrium constant (K_{ex}) is found to be independent of the solvent. Acid dissociation constant of the reagent LIX 63 is determined from 70% (vol/vol) ethanol-water medium and the overall extraction is predicted to be independent of the nature of solvent.

The successful commercial development of high molecular weight hydroxy oxime series of copper-selective extractants[1,2] has led to much interest in the chemistry of transition metal-hydroxy oxime systems. Equilibrium behaviour as well as kinetics of the extraction of copper(II) with 5,8-diethyl-7-hydroxydodecan-6-one oxime (LIX 63) in chloroform has been reported[3].

The existing methods of hydrometallurgical extraction of platinum group metals often present difficulties due to the slow rate of formation of the extractable complexes from aqueous chloride medium[4]. However, because of the strong tendency of palladium to form chloro complexes in aqueous solutions, its extraction with LIX 63 seems to be interesting because of the higher selectivity with respect to the base metals and platinum and also for the higher acidity that it can tolerate for the complete extraction.

Materials and Methods

Absorbances were recorded using a Shimadzu Graphicord UV 240 spectrophotometer. All pH measurements were made with a Systronics 335 digital pH meter, calibrated daily with buffer solutions of pH 2.00, 4.00 and 7.00. A box type Sambros reciprocating shaker with a shaking speed of 200 oscillations per minute was used to equilibrate the aqueous and organic phases, whenever needed.

A stock solution of palladium (5.65×10^{-2} M) was prepared by dissolving palladium(II) chloride (Johnson-Mathey, 99.9% purity) in 1 M hydrochloric acid. It was standardised gravimetrically by dimethyl glyoxime. 5,8-Diethyl-7-hydroxydodecan-6-one oxime, commercially available as LIX 63, was kindly supplied by Henkel Corporation, Tucson, Arizona in the undiluted form. All other reagents used were of AR grade. Organic diluents used for the extraction studies were distilled twice and were presaturated with water whenever required.

Extraction procedure for determination of K_{DR}

For determination of the distribution constants (K_{DR}) of the extractant (LIX 63) in different solvents, known amounts of the extractant in 25 ml of the diluent were equilibrated for 4 hr with aqueous phases (750 ml). The aqueous phases were presaturated with the respective diluents and were buffered at pH 5 with acetic acid and sodium acetate; the ionic strength of the aqueous phases was maintained constant (0.1 M) with respect to chloride ion. After equilibration, the concentrations of the extracted ligand were determined spectrophotometrically[5]. K_{DR} values were then calculated.

Extraction procedure for equilibrium studies

The distribution of palladium(II)-LIX 63 complex between aqueous and organic phases was examined as a function of aqueous pH, chloride ion concentration, metal ion concentration and the reagent con-

centration in the bulk organic phase. LIX 63 was dissolved in seven different solvents to form the respective organic phases. A 10 ml portion of aqueous metal solution of known concentration was shaken for 2 hr with equal volume of ligand solution in the desired solvent. The metal concentration in the aqueous phase after the extraction was determined spectrophotometrically by potassium iodide[6] and extracted metal (as Pd-LIX 63 complex) concentration in the organic phase was also determined spectrophotometrically at the wavelength 330 nm against a blank solution, prepared similarly.

Procedure for determination of acid dissociation constant of the extractant

Acid dissociation constant of the extractant was determined by pH-metric titration of 0.01 M nitric acid in absence and in presence of 0.01 M LIX 63 at 30°C in ethanol-water medium (70% volume/volume) (having a constant ionic strength of 0.1 M) against 0.125 M sodium hydroxide solution. pH values were measured with reference to the 70% (v/v) ethanol-water standard state by applying appropriate correction factors[7]. the pK_a value, evaluated by the procedure of Irving and Rossotti[8], was found to be 10.73.

Results and Discussion

Distribution of LIX 63 between organic diluents and water

The distribution ratio D_R of LIX 63 was determined between various organic solvents and water at pH 5 and at temp. 25°C. A small variation in pH (around 5) had no significant effect on D_R.

Distribution ratio (D_R) of a weakly acidic reagent like LIX 63 between organic and aqueous media can be described in terms of its acid dissociation constant (K_a), its Nernst distribution constant (K_{DR}) and, when applicable, its organic phase polymerisation constant, (K_p).

As can be seen from Fig. 1, which summarises the results of the distribution experiments at pH 5, there is no concentration dependence on D_R of the extractant (LIX 63) for chloroform, toluene, dichloromethane and benzene; this signifies that polymer formation does not occur in the examined range of concentration $(10^{-3}\ M\text{-}10^{-2}\ M)$ of LIX 63 in these solvents.

However, in carbon tetrachloride, n-hexane and n-heptane, the D_R values increased with an increase in the concentration of the extractant, probably owing to the self-association. The log K_{DR} values thus obtained in different diluents vary from 3.3 to 5.3 (Table 1, Fig. 1) depending upon the solvent in the following order: n-heptane $<$ n-hexane $<$ carbon te-

Table 1—Extraction parameters of solvent extraction of palladium(II) with LIX 63 in seven organic diluents

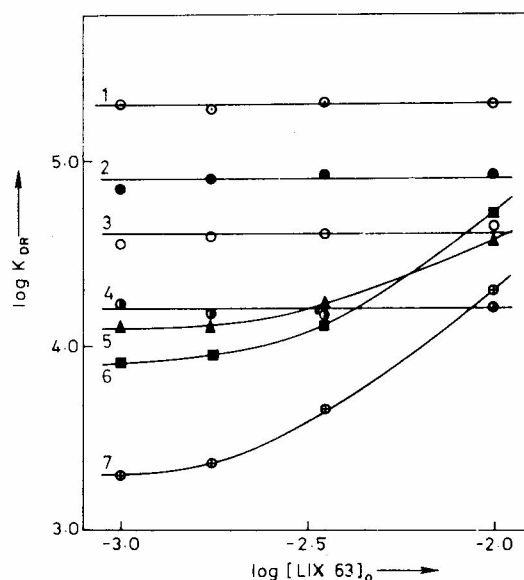| Solvent	Dielectric constant	log K_{DR}	K_{ex}	log K_f K_{DC}
Chloroform	4.806	5.3	1.17	32.13
Toluene	2.438	4.9	0.94	31.23
Dichloromethane	9.08	4.6	0.95	30.64
Benzene	2.284	4.2	1.26	29.96
Carbon tetrachloride	2.238	4.1	1.62	29.87
n-Hexane	1.890	3.9	0.94	29.23
n-Heptane	—	3.3	0.91	27.96

Fig. 1—Distribution constant of LIX 63 between organic solvents and the aqueous phase of pH 5 ($I = 0.1 M$ with NaCl) [1, Chloroform; 2, toluene; 3, dichloromethane; 4, benzene; 5, carbon tetrachloride; 6, n-hexane; 7, n-heptane].

trachloride $<$ benzene $<$ dichloromethane $<$ toluene $<$ chloroform.

It is thus observed from the distribution experiments that the possibility of self-association comes into play for the totally non-polar solvents. With increasing polarity of the solvents, this possibility diminishes, if not disappears completely.

Moreover, the log K_{DR} values of the extraction in different solvents showed an increasing trend with increasing dielectric constant, with a deviation in the case of dichloromethane. This might well be due to the fact that the contribution of the dispersion interaction (δ_d) to the solubility parameter (δ) for dichloromethane is significantly lower in comparison to that for other diluents used.
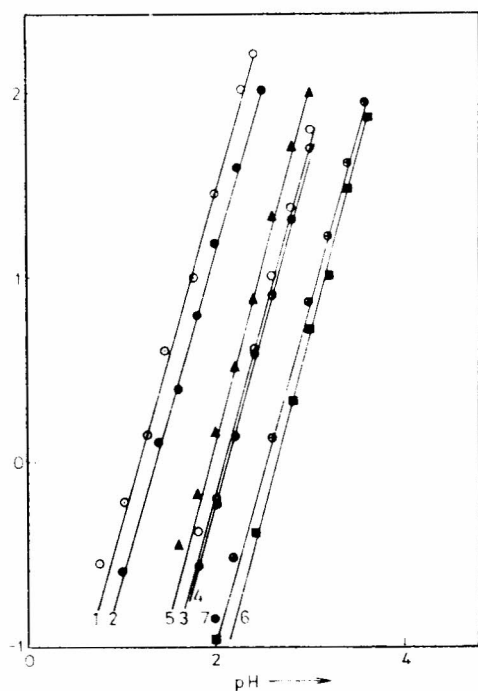
Fig. 2—Distribution ratio of palladium(II) as a function of pH at $[HL]_0 = 3.69 \times 10^{-2}$ M [1, chloroform; 2, toluene; 3, dichloromethane; 4, benzene; 5, carbon tetrachloride; 6, n-hexane; 7, benzene].

Fig. 3—Distribution ratio of palladium(II) as a function of LIX 63 concentration in the organic solvents [1, Chloroform pH 2.4; 2, toluene pH 2.5; 3, dichloromethane pH 3.0; 4, carbon tetrachloride pH 3.0; 5, benzene pH 3.0; 6, n-hexane pH 3.6; 7, n-heptane pH 3.6].

Extraction of palladium with LIX 63

The distribution ratio of the metal (D_{Pd}) as a function of LIX 63 concentration in the bulk organic phase and of aqueous metal ion concentration, chloride ion concentration and pH was determined. The distribution ratio of the metal was found to be independent of the aqueous chloride ion concentration in the $[Cl^-]$ range 0.005 M to 0.1 M and of the metal ion concentration as well, indicating that extraction of any polymeric species involving the metal is non-operative.

The log D_{Pd} vs pH plots at a constant extractant concentration and at a constant ionic strength (0.1 M with respect to chloride ion) of the aqueous phases yield a straight line (Fig. 2) with slopes nearly equal to two in each of the solvent systems. The analogous log D_{Pd} vs log $[LIX\ 63]_0$ plots at constant pH were also linear with slopes of around two in all of the diluents used (Fig. 3). These results indicate that a simple 1:2 (metal:ligand) chelate is extracted in the organic phase. The consistency of the K_{ex} values (~ 1) obtained from the corresponding log D_{Pd} vs log $[LIX63]_0$ plots for different solvents confirms that the overall extraction constant is independent of the nature of the solvents and a single metal species with identical stoichiometry is extracted in all the seven different organic diluents used. The line-
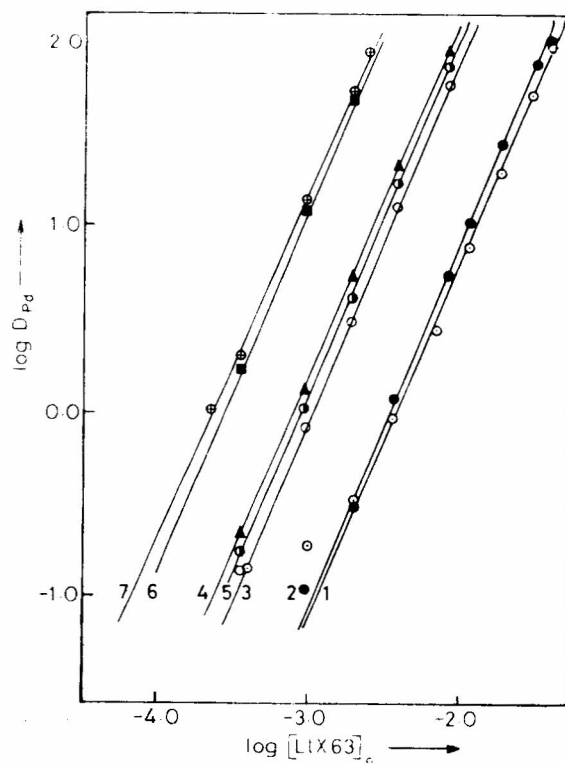
arity obtained in Figs 2 and 3 and the consistency of the slope values for the curves of different systems clearly indicate that self-association of the reagent (LIX 63) in carbon tetrachloride, n-hexane and n-heptane hardly has any significant effect on the overall metal-chelate-extraction systems.

Effect of solvent on extraction equilibria

Acid dissociation constant (K_a) of the reagent and the formation constant (K_f) of the complex are expected to be independent of the organic phase in extraction system, as they primarily are aqueous phase constants. On the other hand, the K_{DC} could be affected by the nature of the organic solvent. Solvent influence and hence the change in the distribution constants K_{DR} and K_{DC} is predictable from the extra-thermodynamic linear free energy relationship of Hansch and Leo[9]. When this approach is used, two hypotheses are to be applied. Firstly, if a simple chelate is extracted, the variation in the distribution constant of the metal chelate with solvent is related to the distribution constant of the ligand by the equation:

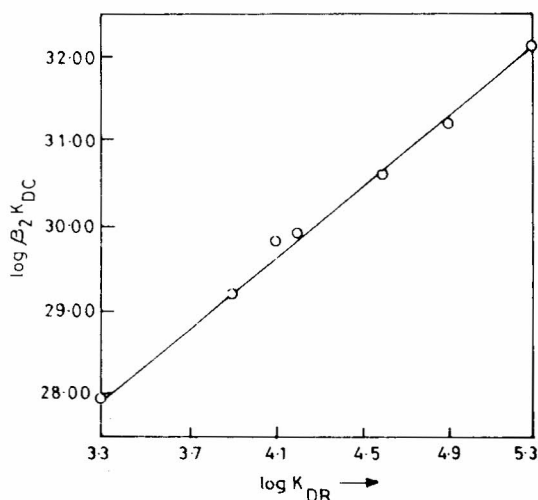$$\log K_{DC} = n \log K_{DR} + C \qquad \qquad \ldots (1)$$

Fig. 4—Correlation between the distribution constant of LIX 63 and of its palladium-LIX 63 chelate.

where, C is a constant, accounting for other extraction parameters and 'n' is the number of ligand molecules bound to the central metal. Secondly, in systems where Eq. (1) holds good, the extraction constant will be essentially independent of the organic diluents. Hence, irregularities or deviations from the linearity in the curve, obtainable from Eq. (1), will suggest the possibility of stoichiometric dif-

ferences in the extracted species in different solvents and/or existence of specific solvation effect. Fig. 4 illustrates the solvent effect where $\log K_f K_{DC}$ are plotted against $\log K_{DR}$ values of the reagent (LIX 63) for respective organic diluents. Considering K_f as an organic phase-independent parameter, all variations in $K_f K_{DC}$ can be attributed to that in K_{DC} only. A reasonably good linear relationship between the two parameters (K_{DC} and K_{DR}) with a slope of two (Fig. 4) rules out any stoichiometric differences amongst the extracted species in different organic diluents, and the possibility of any specific solvent effect either. Any evidence of irregular trend had not been observed for the present Pd-LIX 63 complex as was reported in the extraction of copper with LIX 65 N[10].

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