Heavy Metal Ion Extraction Using Organic Solvents: An Application of the Equilibrium Slope Method

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1. Introduction

The separation procedure of a chemical species from a matrix is essentially based on the transportation of the solute between the two involved phases, generally an organic and an inorganic one. Specifically, solvent extraction uses the concept of unique solute distribution ratios between two immiscible solvents. However, there are several situations where solutes have been observed to completely move from the inorganic to the organic phase (Anthemidis and Ioannou, 2009).

Organic solvent extraction is the transport of solutes, e.g. heavy metal ions, from an inorganic (or aqueous) phase to an organic phase. Solvents used comprise of an extractant + diluent combination. The roles of each are as follows: 1) the extractant, as a specific metal ion extractant; 2) the diluent, as a solvent condition controller, i.e. hydrophobicity, which can affect the molecules extractability (Watson, 1999; Cox, 2004). Occasionally, a phase modifier can be added to solve the problem of emulsion formation, aside from improving the phase demarcation process in an aqueous organic system (Cox, 2008).

Solvent extraction is widely applied to processes of metal ions recovery, ranging from aqueous solutions in hydrometallurgical treatment to environmental applications. It is also considered a useful technique to increase the initial concentration of the solute, commonly used in the separation processes of analytical applications (Reddy et al., 2005).

In the biomedical field, supported liquid membrane methodology was used for trace analytes determination by facilitating chromatogram differentiation between samples, water and blood plasma (Jonsson and Mathiasson, 1999). It is also used to enrich human wastes (e.g. urine) with heavy metals prior to concentration determination using atomic absorption spectroscopy (AAS) (Lindegrade et al., 1992; Djane et al., 1997a; Djane et al., 1997b).

1.1 Organic solvents

Numerous organic solvents have been utilized to remove heavy metals (Leopold et al., 2010; Rafighi et al., 2010; Chang et al., 2011; Fu et al., 2011; Mishra and Devi, 2011). Most of them are, in part, made from petroleum. Recently, solvents such as vegetable oil (Venkateswaran

et al., 2007; Chang et al., 2010), were exploited as alternatives to replace the commonly used petroleum-based organic solvents. Additionally, a family of “specialist” extractants, known as the organo-phosphorous compounds, are also employed as metal extractants (Sainz-Diaz et al., 1996).

Some examples of solvents applied in heavy metals extraction are:

- Di-2-ethylhexylphosphoric acid (D2EHPA), extensively used as an extractant for the separation of Cu(II) from aqueous solutions (Gherrou et al., 2002; Ren et al., 2007; Cox, 2008). Other applications of this popular extractant include the removal of Cd(II) (Kumar et al., 2009), Zn(II) (Vahidi et al., 2009), Fe(III) and Ti(IV) (Silva et al., 2008);
- Tributylphosphate (TBP), used to act as a phase modifier in Cu(II) extraction (Cheng, 2000). The extractant and phase modifier are diluted at certain ratios in the petroleum-based organic diluents such as kerosene and chloroform (Ak et al., 2008; Ren et al., 2008), cumene (Svendsen et al., 1990), dichloromethane (Memon et al., 2003), isododecane (Mortes and Bart, 2000), n-dodecane (Simonin et al., 2003), n-decanol (Lin et al., 2005), n-heptane (Morais and Mansur, 2004), and n-hexane (Valenzuela et al., 2002);
- LIX 84 and Cyanex 272, applied to extract Cu(II), Ni(II), and Al(III) (Mohapatra et al., 2007; Agrawal et al., 2008);
- Cyanex 921, used to extract Cu(II) from HCl (Mishra and Devi, 2011);
- Miscellaneous organic solvents such as I) 1-phenyl-3-heptyl-1,3-propanedione, II) 1-phenyl-4-ethyl-1,3-octanedione, III) 1-(4'-dodecyl) phenyl-3-tert-butyl-1,3-propanedione in kerosene, used to extract Cu(II) (Fu et al., 2011).

2. Stoichiometry of heavy metals extracted using organic solvents: Equilibrium slope method

The equilibrium slope method has been used by many researchers to determine the stoichiometry of various metal-organic complexes in organic solvents (Nagaosa and Yao, 1997; Wang and Nagaosa, 2001; Mansur et al., 2002; Kumar et al., 2009). Most of its applications deal with extracting metal ions from aqueous solutions. It has proven a very useful technique of its ease of use, and its accuracy when validated by other methods, such as numerical and quantitative analysis from Fourier Transform Infrared Spectroscopy (FTIR).

2.1 General equilibrium slope methodology

Following this methodology, the extractant form in the organic solvent would need to be estimated first. Subsequently, the formulation of a balanced reaction equation would be derived. A general form of the reaction equation is shown below (Eq. 1). Some applied assumptions include that the solubility of the extractant and the metal-extractant complex in the aqueous phase is small, and that the extracted metal ions are not associated to one another.

where,

- M = metal ion
- R = hydrocarbon group
- n = oxidation number
- x = stoichiometric coefficient
- $_{org}$ = organic phase
- K_{eq} = equilibrium constant

The equilibrium constant, K_{eq} , can be experimentally determined. In turn, K_{eq} is a function of D_{eq} , which is the equilibrium distribution ratio of the metal ion concentration in the organic and the aqueous phase (Eq. 2).

$$D_{eq} = \left(\frac{M^{n+}_{(org)}}{M^{n+}_{(aq)}} \right)_{eq} \quad (2)$$

During the experiment, the ionic strength and the correlated activity coefficient, a , is needed to be kept constant by adding inert chemicals or substances such as salts. A plot of $\lg D_{eq}$ against pH_{eq} can be drawn to determine the valency of the extracted metal ion. This information can also be used to ensure the experiment validity by cross-checking the actual valency of the studied metal ion to the slope of the drawn plot. In addition, a plot of $\lg D_{eq}$ versus $\lg [\text{extractant}]$, will reveal the value of the stoichiometric coefficient of the extractant, x .

2.2 Application of the equilibrium slope methodology

In this section a separated study on the equilibrium slope method applied to different metal ions reported in literature is presented.

2.2.1 Cu (II)

Cu(II) extraction from aqueous solutions using different organic solvents have been studied extensively. Combination of extractants and solvents used to extract Cu(II) from an aqueous solution in literature include D2EHPA + soybean oil (Chang et al., 2010; Chang et al., 2011), LIX 84 + kerosene (Agrawal et al., 2008), Cyanex 921 + kerosene (Leopold et al., 2010; Mishra and Devi, 2011), and Cyanex 272 + kerosene (Mohapatra et al., 2007; Agrawal et al., 2008; St John et al., 2010). The solvents employed are mostly non-polar in nature.

The steps required to determine the stoichiometric coefficient of the extractant are somewhat similar between the extractant + solvent combinations. Thus, the general technique, in sequence, is listed below.

The relevant reaction equation can be written as Eq. (3), where K_{eq} is defined as Eq. (4) and Eq. (5).

where,

$$K_{eq} = \frac{[\text{CuR}_x][\text{H}^+]^x}{[\text{Cu}^{2+}][\text{HR}]^x} \quad (4)$$

$$D_{eq} = \left(\frac{Cu^{2+}_{(org)}}{Cu^{2+}_{(aq)}} \right)_{eq} \quad (5)$$

By substituting Eq. (5) into Eq. (4),

$$K_{eq} = D_{eq} \frac{[H^+]^x}{[HR]^x} \quad (6)$$

$$K_{eq}[HR]^x = D_{eq}[H^+]^x \quad (7)$$

$$\lg K_{eq} + x \lg [HR] = \lg D_{eq} + x \lg [H^+] \quad (8)$$

Since,

$$x \lg [H^+] = -x p H_{eq} \quad (9)$$

Hence,

$$\lg D_{eq} = x p H_{eq} + \lg K_{eq} + x \lg [HR] \quad (10)$$

A plot of $\lg D_{eq}$ versus $p H_{eq}$ is illustrated in Fig. 1. A summary of published slope and intercept values is listed in Table 1. It can be deduced that the stoichiometric coefficient would generally equal to the charge of the metal ion extracted.

Fig. 1. $\lg D_{eq}$ versus $p H_{eq}$

Extractant + solvent	x	$\lg K_{eq} + x \lg[HR]$	Extractant formula with metal	Reference
D2EHPA + soybean	1.99	-7.12	$\text{CuR}_2(\text{HR})_2$	Chang et al. (2011)
LIX 84 + kerosene	1.5133	-0.9 (estimated)	CuR_2	Agrawal et al. (2008)
Cyanex 921 + kerosene	2.249	-1.6105	CuR_2	Mishra and Devi (2011)
Cyanex 272 + kerosene	1.75	-1 (estimated)	CuR_2	Agrawal et al. (2008)

Table 1. Slope and intercept of $\lg D_{eq}$ versus pH_{eq}

An average of $1.88 \approx 2$ for the slope has been observed by researchers using non-polar solvents. According to Chang et al. (2011), the Cu(II) ions were solvated by two simple molecules of D2EHPA, a supposition that stem from the slope obtained using the equilibrium slope method. In conclusion, the number of molecules of the extractant $(\text{HR})_x$ (or R) determined by all researchers was unanimously 2, even when using different extractant and diluent combinations.

2.2.2 Ni (II)

Since Ni(II) has the same oxidation number as Cu(II) and not much work has been published on the extraction of this metal ion, then it can be assumed that Ni(II) would behave as Cu(II) would. A precaution when using this assumption is the type of solvent + extractant combination, which would give variable results on slope and intercept values. These values, in turn, depend on empirical or experimental values. The general reaction equation is written as Eq. (11) and the equilibrium constant as Eq. (12).

$$K_{eq} = \frac{[\text{NiR}_x][\text{H}^+]^x}{[\text{Ni}^{2+}][\text{HR}]^x} \quad (12)$$

The results obtained is similar to what has been developed for Cu(II). This is supported by Tanaka and Alam (2011), which obtained a slope of 2 for pH between 1 and 4. Moreover, they found that for Ni(II), the $\lg D_{eq}$ versus pH diagram would exhibit 3 regions: I) $\text{pH} < 4$; II) $5 < \text{pH} \leq 8$; and III) $\text{pH} > 8$ (refer to Figure 2). It was also discovered by the latter researchers that at higher initial concentrations of LIX84I, another extractant, would extend the line with slope 2 until a pH of approximately 5.

In the $\text{pH} < 4$ region, the slope of the $\lg D$ versus pH curve would be 2 and the Ni(II) ions would exist as free ions. Thus, the extraction process would result from the ion exchange interaction between Ni(II) and 2H^+ (same as Cu(II)). For $5 < \text{pH} \leq 8$, the slope would be virtually zero and the organic phase would be saturated with the Ni(II) ions. However, Ni(II) ions can still be extracted through proton exchange by forming the compound, NiR_2 (similar to Cu(II)). Still, the pH needs to be adjusted to achieve this. In the third region, $\text{pH} > 8$, the slope would essentially be negative (in this case of extracting Ni(II) from ammonium solutions) because of the formation of nickel-ammine complexes occurring concurrently with the decrease in free Ni(II) ion concentrations (Agrawal et al., 2008).

Fig. 2. $\lg D_{eq}$ as a function of pH at equilibrium

2.2.3 Cd(II)

A dimer formation between Cd(II) ions and an organic group has been suggested by many researchers (Kumar et al., 2009). Thus, the mechanism of extraction of Cd(II) with organic solvents would also behave the same as Cu(II) and Ni(II), as previously discussed. Since the researchers postulated a molecular form of the resulting organic complex, they could formulate a specific chemical reaction equation, written as Eq. (13). In the specific case of using D2EHPA + kerosene to extract this metal ion, the researchers have found a slope of 1.9143 and y-intercept of 4.5132 between the pH range of 1 and 5.

where,

p = number of molecules of extractant engaged in reaction

Parrus et al. (2011) plotted a $\lg D_{eq}$ versus $\lg$ [extractant] graph to determine the number of organic molecules attached to Cd(II) following the application of the equilibrium slope method using 1-(2-pyridyl)-tridecan-1-one and 1-(2-pyridyl)-pentadecan-1-ol oximes in chloroform. They found that the slopes are, on average, 2, corroborating the postulate of the previous researchers on the molecular structure of the Cd(II) organic complex.

2.2.4 Cr(III)

Using the general reaction equation given by Eq. (1) and the steps applied on Cu(II), the relevant resulting equations are written below (Eq. 14-19).

where,

$$K_{eq} = \frac{[CrR_x][H^+]^x}{[Cr^{3+}][HR]^x} \quad (15)$$

$$D_{eq} = \left(\frac{Cr^{3+}_{(org)}}{Cr^{3+}_{(aq)}} \right)_{eq} \quad (16)$$

By substituting Eq. (16) into Eq. (15),

$$K_{eq} = D_{eq} \frac{[H^+]^x}{[HR]^x} \quad (17)$$

$$K_{eq}[HR]^x = D_{eq}[H^+]^x \quad (18)$$

Hence,

$$\lg D_{eq} = x p H_{eq} + \lg K_{eq} + x \lg [HR] \quad (19)$$

Researchers (Al-Zoubi et al., 2011) have found that for their situation, i.e. a combination of Cu(II) and Cr(III) ions in an aqueous solution, only Cu(II) is the extractable species. A linear relationship was still observed for Cu(II) and Cr(III) with a slope of 2 and 0.68, respectively.

2.2.5 Zn(II)

Baba and Adekola (2011) proposed the general reaction equation, Eq. (1), for metals Zn, Cd, Co, Fe, Pb, Ca, and Mg when using D2EHPA. They stated that the extraction process depends on solution composition, equilibrium, pH, and type of diluents, while the increase in proton concentrations would further promote this reaction. Mellah and Benarchour (2006) proposed a specific reaction equation for Zn(II) when extracting it using D2EHPA written as Eq. (20) based on the assumptions that extractant molecules exist as dimers in the solvent (kerosene in their work). They obtained a slope of 1.7152 and 1.7153 for 0.1 M and 0.2 M of D2EHPA, respectively.

Since the general reaction equation is applicable for Zn(II) and shown by Baba and Adekola (2011) as well, a slope of approximately 2 would be evident from the $\lg D_{eq}$ versus pH plot. The latter authors reported a slope of 1.86. Li et al. (2003) has also reported a close to 2 value of 1.92 when extracting Zn(II) using Cyanex 272

2.2.6 U(VI)

Even though the oxidation number of U(VI) is more than 2, in the work published by St John et al. (2010) it was found that the slope of the $\lg D_{eq}$ versus pH plot is 2.10. This is due to U(VI) forming a complex with O_2 that results in the formation of UO_2^{2+} , thus the equilibrium slope of 2.

2.2.7 Co(II)

The reaction equation and the related equilibrium constant for the extraction of Co(II) using Cyanex 272 are written as Eq. (21-25) (Parhi et al., 2008). A slope of 2.0282 was obtained, proving that the extracted species was CoR_2 .

where,

$$K_{eq} = \frac{[\text{CoR}_x][\text{H}^+]^x}{[\text{Co}^{2+}][\text{HR}]^x} \quad (22)$$

$$D_{eq} = \left(\frac{\text{Co}^{2+}_{(org)}}{\text{Co}^{2+}_{(aq)}} \right)_{eq} \quad (23)$$

By substituting Eq. (23) into Eq. (22),

$$K_{eq}[\text{HR}]^x = D_{eq}[\text{H}^+]^x \quad (24)$$

Hence,

$$\lg D_{eq} = x\text{pH}_{eq} + \lg K_{eq} + x\lg[\text{HR}] \quad (25)$$

In another study by Rafighi et al. (2010), a different reaction equation was proposed (Eq. 26) Plots of $\lg D_{eq}$ versus $\lg$ [extractant] showed slopes of 1 and 2, pertaining to the number of organic molecules attached to Co(II).

2.2.8 Al(III)

In a paper by Mohapatra et al. (2007), Al(III) was extracted using Na-Cyanex 272 and Na-D2EHPA. The slopes of the $\lg D_{eq}$ versus pH are 1.85 and 2.40 for the two solvents, respectively. The reaction equation is written below (Eq. 27-31). Notice the stoichiometric coefficient of H^+ is 3.

$$K_{eq} = \frac{[\text{AlH}_{2n-3}\text{R}_{2n}][\text{H}^+]^3}{[\text{Al}^{3+}][\text{HR}]_2^n} \quad (28)$$

$$K_{eq} = \frac{D_{eq}[\text{H}^+]^3}{[\text{HR}]_2^n} \quad (29)$$

where,

$$D_{eq} = \frac{[\text{AlH}_{2n-3}\text{R}_{2n}]}{[\text{Al}^{3+}]} \quad (30)$$

Hence,

$$\lg D_{eq} = \lg K_{eq} + n\lg[\text{HR}]_2 - 3\lg[\text{H}^+] \quad (31)$$

3. Other methods to determine stoichiometry of heavy metals extraction using organic solvents

There are other methods that can be used to validate the stoichiometry of the organic complexes produced from the heavy metal extraction process using organic solvents. These methods include numerical analysis and quantitative analysis using FTIR.

Numerical analysis requires that a multiple regression analysis be conducted using a first order function, written as Eq. (32).

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \varepsilon \quad (32)$$

where,

- β_0 = constant for intercept
- β_i = constant for linear variables
- y = dependent variable
- x_i = independent variable
- ε = error term

This is followed by a best fit exercise using the least square method. As an example, albeit a very specific one and since this analysis is highly empirical in nature, constants can be estimated, along with the corresponding standard deviation, t and probability (P) values, for the variable terms of a regression model of $\log D_{eq}$. At a 5% significance level, all variable terms, when found to have $P < 0.05$, are thus considered statistically significant. Hence, a first-order polynomial model that correlates $\log D_{eq}$ with all the variable terms can be developed.

The adequacy or goodness of fit of the regression model can be analyzed using analysis of variance (ANOVA) at a 5% significance level. Low P ($P < 0.05$) value of the regression model indicates that it is statistically significant. To test the global fit of the model, the coefficient of determination (r^2) can also be evaluated. Small deviations between the r^2 and adjusted r^2 values would imply that there is less chance for the inclusion of any insignificant terms in the model and that the model is highly significant.

Since Eqs. (32) and (10) are of the same forms, their constants for each variable term can be compared conveniently. By evaluating the constants of $\log[(HR)_2]$ from Eq. (4), i.e. $(2+m)/2$, with that from the regression model, the m value can be determined and, thus, brings about the stoichiometric ratio.

Chang et al. (2011) has used this method to confirm that the slope of the $\lg D_{eq}$ versus pH is 2 (= 1.988).

Quantitative analysis using FTIR requires an FTIR analysis of the metal ion-loaded organic solvent. This is detailed in the paper by Sainz-Diaz et al. (1996). For the case of Cu(II) and D2EHPA, it leverages the fact that there is a highly polar phosphoryl bond (P=O) in the D2EHPA compound and could easily react with Cu(II). Knowing that the absorbance of the P=O band is at 1235 cm^{-1} at multiple concentrations of D2EHPA standard solutions, a calibration curve can be obtained. This calibration curve can be used to determine the concentration of D2EHPA that did not react with Cu(II). By finding the difference between the reacted and unreacted concentrations of D2EHPA, the concentration of Cu-D2EHPA (organic complex) can be estimated. A plot of the Cu-D2EHPA versus the organic concentration of Cu will reveal the slope that corresponds to the constant stoichiometric ratio of D2EHPA.

4. Conclusion

Liquid extraction of heavy metals is widely applied in many fields ranging from the environmental to the biomedical discipline. In the environmental field, some of the more prominent applications include: removal and recovery of heavy metals and dyes from wastewater. In the biomedical field, liquid extraction has been used in the determination of heavy metals in human waste (e.g. urine). However, trace analytes extraction is still a great challenge in the pharmaceutical and medical industry.

In this chapter, the equilibrium slope method and its utility in estimating the stoichiometry of the resulting organic complexes has been reviewed for multiple heavy metal ions. The number of protons involved generally dictates the slope of the $\lg D_{eq}$ versus pH plot. A slope of 2 is common for many heavy metals, thus attributing that the general organic complexes obtained from these extraction processes are in the form of dimers.

In brief other methods, numerical and FTIR quantitative analysis have been discussed and might be helpful to further corroborate the results of the equilibrium slope method.

5. References

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Stoichiometry and Research - The Importance of Quantity in Biomedicine

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The aim of this book is to provide an overview of the importance of stoichiometry in the biomedical field. It proposes a collection of selected research articles and reviews which provide up-to-date information related to stoichiometry at various levels. The first section deals with host-guest chemistry, focusing on selected calixarenes, cyclodextrins and crown ethers derivatives. In the second and third sections the book presents some issues concerning stoichiometry of metal complexes and lipids and polymers architecture. The fourth section aims to clarify the role of stoichiometry in the determination of protein interactions, while in the fifth section some selected experimental techniques applied to specific systems are introduced. The last section of the book is an attempt at showing some interesting connections between biomedicine and the environment, introducing the concept of biological stoichiometry. On this basis, the present volume would definitely be an ideal source of scientific information to researchers and scientists involved in biomedicine, biochemistry and other areas involving stoichiometry evaluation.

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