LIQUID-LIQUID EXTRACTION OF TRANSITION METAL CATIONS BY GLYOXIMES

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Abstract

*Liquid-liquid extraction **of varied** alkalis (Li^+, Na^+, K^+, and $C_s{}^+$), transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), and Pb^{2+} cations with phenylglyoxime (L1), p-tolylglyoxime (L2), N'-(4'-Benzo[15-crown-5]) phenylaminoglyoxime (L3), and N'-(4'-Benzo[15-crown-5])-p-tolylaminoglyoxime (L4) from the aqueous phase into the organic phase was **dole out**. For comparison, the corresponding two glyoximes and their macrocyclic glyoxime ether derivatives were also examined. Crown ether groups having ligands (L3, L4) carry especially Na^+ cation from aqueous phase to organic phase. The extraction equilibrium constants (Kex) for complexes of ligands with Cu^{2+} and Hg^{2+} metal picrates between dichloromethane and water **are** determined at 25°C. The values of the extraction constants (logKex) were determined to be 12.27, 13.37, 12.94, and 12.39 for Cu2+ and 10.29, 10.62, 11.53, and 11.97 for Hg^{2+} with L1–L4, respectively.*

Keywords: *Solvent, Liquid Extraction, Metal, salts, Cations, Glyoximes*

Introduction

Oxygen-containing macrocycles compounds **are** used extensively in extraction, **thanks to the wonderful** compatibility between the crown-ring sizes **and therefore the** ionic radii of metals. Solvent extraction with crown ethers **may be a** suitable method for metal analysis **due to** their high selectivity and affinity towards specific metals. The **Kekule formula** introduces much higher lipophilicity of crown ether than the cyclohexyl ring does **in line with** their distribution ratios [1, 2]. In addition, other pendent substituents on the crown ring also improve the lipophilicity [3].

Crown ethers **are** found to be powerful extracting agents for **alkaline metal** salts [4]. **They're** also accepted to be model compounds to mimic antibiotics in cation transport through lipid membranes [5].

The existence of both mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes -dioximes amphoteric ligands which form corrin-type square planar, square pyramidal, and

octahedral complexes with nickel(II), cobalt(II), copper(II), palladium(II), and cobalt(III) as central metal atoms.

We check here a comparison of the solvent extractions of metal ions (Li^+, Na^+, K^+, C_s^+, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) by the glyoxime and their macrocyclic glyoxime ether derivatives.

Experimental

Chemicals and Equipment

Figure 1 shows the formula of L1–L4. Phenylglyoxime (L1) [12, 13], p-tolylglyoxime (L2) [14], N′-(4′-Benzo[15-crown-5])phenylaminoglyoxime (L3) [9], and N′-(4′-Benzo[15-crown-5])-p-tolylaminoglyoxime (L4) [10] were prepared per published methods. All reagents used in the experiments were purchased from Merck (Germany) and were used without extra purification. All aqueous solutions were prepared with deionized water that had been had a Millipore Milli-Q Plus water purification system. UV/VIS spectra were recorded on a Shimadzu 160A spectrometer.
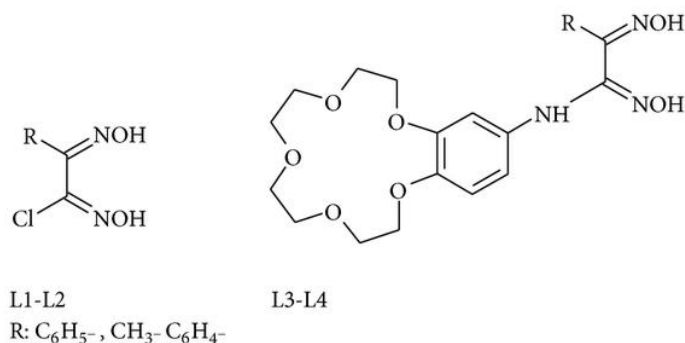

Figure 1 Formula of L1–L4.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure [18]. 10 mL of a 2.10^{-5} M aqueous picrate solution and 10 mL 1.10^{-3} M solution of ligand in CH2Cl2 were vigorously agitated **in a very** stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred **in a very** thermostated water bath at 25°C for 1 h, **and eventually** left standing for **an extra** 30 min. The concentration of the picrate ion remaining **within the** aqueous phase was then determined spectrophotometrically, as previously described [19]. Blank experiments showed that no picrate extraction occurred **within the** absence of ligand. The alkali picrates were prepared as described elsewhere [19] by stepwise addition of a

2.10^{-2} M aqueous **acid** solution to a 0.14 M **solution** of **metallic element** hydroxide until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried in vacuo for 24 h. Transition metal picrates were prepared by successive addition of a 1.10^{-2} M metal nitrate solution to 2.10^{-5} M aqueous **acid** solution and shaken at 25°C for 1 h. These metal picrates (Li$^+$, Na$^+$, K$^+$, Cs$^+$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) were measured by UV using does maximum wavelength (357, 349, 349, 349, 349, 361, 349, 357, 349, 349, and 346 nm). The extractability of the metal cations is expressed by means of **the subsequent** equation (1):

$$\text{Extractability } (\%) = \left[\frac{A_0 - A}{A_0}\right] \times 100, \tag{1}$$

where A_0 and A are the absorbencies in the absence and presence of ligands, respectively.

Log-Log Plot Analyses

To characterize the extraction ability, the dependence of the distribution coefficient D of the cation between **the 2** phases on the ligand concentration was examined. If **the final** extraction equilibrium is given by (2).

$$\text{M}^{n+}_{(aq)} + n\text{Pic}^-_{(aq)} + x[\text{L}]_{(org)} \longrightarrow [\text{M(Pic)}_n(\text{L})_x]_{(org)}, \tag{2}$$
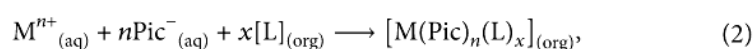
the overall extraction equilibrium constant is

$$K_{ex} = \frac{[\text{M(Pic)}_n(\text{L})_x]}{[\text{M}^{n+}][\text{Pic}^-]^n[\text{L}]^x}, \tag{3}$$

and the distribution ratio D is defined by

$$D = \frac{[\text{M(Pic)}_n(\text{L})_x]}{[(\text{M}^{n+})]}. \tag{4}$$

By introducing D into (4) and taking logarithm of both sides, (5) is obtained:

$$\log D = \log \left(K_{ex}[\text{Pic}^-]^n\right) + x \log [\text{L}]. \tag{5}$$

Under these assumptions, a plot of versus should be linear and its slope should be **up to the amount** of ligand molecules per metal cation **within the** extracted species.

Result and Discussion

Although numerous investigations **are** recently reported regarding the extraction of alkali metals and transition metals from aqueous phase into an organic phase by crown ether [20–23], as yet, reports on solvent extraction with the complexes of oxime compounds were scarce [24–30]. Therefore, **we've** investigated the solvent extraction of metal cations through

crown ether-based oxime compounds. **during this** work, **we've got** investigated the effectiveness **of 4** glyoxime derivatives in transferring the **metallic element** cations (Li$^+$, Na$^+$, K$^+$, and Cs$^+$), transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), and Pb^{2+} cation **in several** pH (Table 1) from the aqueous phase to the organic phase (Tables 2, 3, 4, 5, and 6). Figure 1 illustrates the formulas of the extractants used (L1–L4) **during this** study.

Table 1

Metal picrates and medium pH used in extraction.

Metals	$\cong$ pH	Ni^{+2}	Co^{+2}	Cu^{+2}	Zn^{+2}	Cd^{+2}	Pb^{+2}	Hg^{+2}
pH	2,00	2,17	2,01	2,03	2,07	2,01	2,11	2,11
	3,00	3,00	2,99	3,01	2,99	2,94	3,01	3,06
	4,00	4,00	3,64	4,02	3,92	3,81	4,18	3,95
	5,00	4,77	4,72	4,80	4,95	4,74	4,80	4,96

Table 2

Extraction of metal cations with L1 (%).

Metals	% Extraction			
	pH $\cong$ 2,00	pH $\cong$ 3,00	pH $\cong$ 4,00	pH $\cong$ 5,00
Ni^{+2}	54,54 $\pm$ 0,81	12,74 $\pm$ 0,45	4,50 $\pm$ 0,36	5,67 $\pm$ 0,40
Co^{+2}	71,33 $\pm$ 0,32	24,29 $\pm$ 0,24	1,00 $\pm$ 0,09	10,12 $\pm$ 0,18
Cu^{+2}	67,46 $\pm$ 0,29	42,89 $\pm$ 0,69	63,61 $\pm$ 0,86	70,44 $\pm$ 1,01
Zn^{+2}	65,61 $\pm$ 0,46	11,37 $\pm$ 0,34	1,47 $\pm$ 0,17	1,16 $\pm$ 0,15
Cd^{+2}	71,00 $\pm$ 0,12	22,91 $\pm$ 0,38	7,32 $\pm$ 0,28	3,66 $\pm$ 0,12
Pb^{+2}	63,42 $\pm$ 1,06	24,06 $\pm$ 0,11	6,62 $\pm$ 0,16	5,74 $\pm$ 0,17
Hg^{+2}	46,38 $\pm$ 0,17	21,20 $\pm$ 0,20	20,93 $\pm$ 0,19	13,33 $\pm$ 0,18

[a]H$_2$O/CH$_2$Cl$_2$ = 10/10 (v/v); [picric acid] = 2 $\times$ 10^{-5} M, [ligand] = 1 $\times$ 10^{-3} M, and [metal nitrate] = 1 $\times$ 10^{-2} M, 298 K, 1 h contact time. Averages and standard deviations calculated for data are obtained from five independent extraction experiments.

Table 3

Extraction of metal cations with L2 (%).

Metals	% Extraction			
	$pH \cong 2,00$	$pH \cong 3,00$	$pH \cong 4,00$	$pH \cong 5,00$
Ni^{+2}	$59,84 \pm 0,62$	$18,27 \pm 0,55$	$7,80 \pm 0,14$	$4,54 \pm 0,21$
Co^{+2}	$70,84 \pm 0,96$	$21,67 \pm 0,29$	$10,69 \pm 0,26$	$12,88 \pm 0,31$
Cu^{+2}	$65,97 \pm 0,35$	$94,61 \pm 1,44$	$97,28 \pm 1,73$	$97,63 \pm 1,58$
Zn^{+2}	$68,54 \pm 0,91$	$16,70 \pm 0,19$	$0,1 \pm 0,09$	$0,1 \pm 0,08$
Cd^{+2}	$68,00 \pm 0,46$	$22,91 \pm 0,64$	$7,55 \pm 0,11$	$1,50 \pm 0,10$
Pb^{+2}	$64,21 \pm 1,16$	$19,30 \pm 0,39$	$7,10 \pm 0,26$	$3,99 \pm 0,36$
Hg^{+2}	$66,48 \pm 1,30$	$63,90 \pm 1,89$	$45,21 \pm 0,94$	$20,18 \pm 0,71$

Table 4

Extraction of metal cations with L3 (%).

Metals	% Extraction			
	$pH \cong 2,00$	$pH \cong 3,00$	$pH \cong 4,00$	$pH \cong 5,00$
Ni^{+2}	$56,59 \pm 0,69$	$15,38 \pm 0,30$	$9,94 \pm 0,39$	$4,31 \pm 0,28$
Co^{+2}	$73,00 \pm 0,88$	$28,73 \pm 0,49$	$20,33 \pm 0,44$	$5,63 \pm 0,19$
Cu^{+2}	$78,28 \pm 1,50$	$80,24 \pm 1,77$	$82,09 \pm 1,82$	$83,66 \pm 1,34$
Zn^{+2}	$49,57 \pm 0,74$	$25,13 \pm 0,65$	$15,88 \pm 0,33$	$14,48 \pm 0,27$
Cd^{+2}	$69,39 \pm 0,84$	$24,51 \pm 0,56$	$10,81 \pm 0,42$	$9,03 \pm 0,57$
Pb^{+2}	$50,83 \pm 0,69$	$20,14 \pm 0,55$	$18,97 \pm 0,68$	$17,79 \pm 0,41$
Hg^{+2}	$76,29 \pm 0,93$	$65,70 \pm 0,81$	$50,12 \pm 0,77$	$20,23 \pm 0,59$

Table 5

Extraction of metal cations with L4 (%).

Metals	% Extraction			
	pH ≅ 2,00	pH ≅ 3,00	pH ≅ 4,00	pH ≅ 5,00
Ni^{+2}	59,34 ± 0,83	70,67 ± 1,19	78,19 ± 1,38	67,35 ± 0,97
Co^{+2}	40,48 ± 0,56	62,62 ± 0,70	69,83 ± 1,03	71,83 ± 1,42
Cu^{+2}	33,13 ± 0,87	72,55 ± 1,74	79,70 ± 1,50	79,16 ± 1,64
Zn^{+2}	56,83 ± 0,26	70,53 ± 0,94	73,46 ± 1,06	78,04 ± 1,23
Cd^{+2}	39,75 ± 0,64	57,99 ± 0,69	70,02 ± 0,87	57,85 ± 0,66
Pb^{+2}	37,63 ± 0,34	56,14 ± 0,75	56,86 ± 0,81	71,32 ± 0,24
Hg^{+2}	74,00 ± 0,28	64,46 ± 0,84	35,76 ± 0,55	30,34 ± 0,73

Table 6

Extraction of alkali metal cations with ligands (L1–L4) (%)[a].

Ligands	% Extraction			
	Li^+	Na^+	K^+	Cs^+
L1	1,12 ± 0,29	1,28 ± 0,26	3,88 ± 0,72	2,18 ± 0,32
L2	<1,00	<1,00	1,37 ± 0,17	2,10 ± 0,14
L3	13,79 ± 1,54	60,82 ± 2,68	31,16 ± 1,06	18,76 ± 0,82
L4	13,68 ± 1,80	64,84 ± 3,02	23,63 ± 2,09	18,09 ± 0,76

[a]$H_2O/CH_2Cl_2 = 10/10$ (v/v); [picric acid] $= 2 \times 10^{-5}$ M, [ligand] $= 1 \times 10^{-3}$ M, and [metal hydroxide] $= 1 \times 10^{-2}$ M, 298 K, 1 h contact time. Averages and standard deviations calculated for data are obtained from five independent extraction experiments.

When tables and graphs are examined, **it had been** found that crown ether groups having oxime groups have greater cation carrying ability. Crown ether cycle includes oxygen atoms which are hard atoms. So metals **like** Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} which are **referred to as** soft metals **don't** have any affinity to extraction. However, C=N and N–O groups on the oxime group that **they're** attached to increases the extraction ability **of those** ligands **thanks to** the soft donor structure of the nitrogen atoms and causes big affinity to metals [18].

2 extracted metals from aqueous phase to organic pH $\cong$ 2 L1 and L2 carry pH **innovate** large amounts. Usually, as seen in Tables 2 **and three** and Figures 2 **and three** extraction to organic phase decreases as pH increases. In Hg^{2+} cation **a rather** less decrease is observed compared to other cations. Only after pH 3, **there's a rise** in Cu^{2+} during extraction to organic phase. **This could ensue** to increasing tendency of metal ions **to make** complex over nitrogen as pH increases. When log D-pH graph is examined, this tendency is clearer. In general, oxime compounds precipitation 5 forms complex. This event pH$\cong$5 at approximately pH **is additionally** observed for Co^{2+} when pH increases from 4 **to 5**. The pH **place** which all the research was carried seems to be the mesh appropriate pH range for having no precipitation.
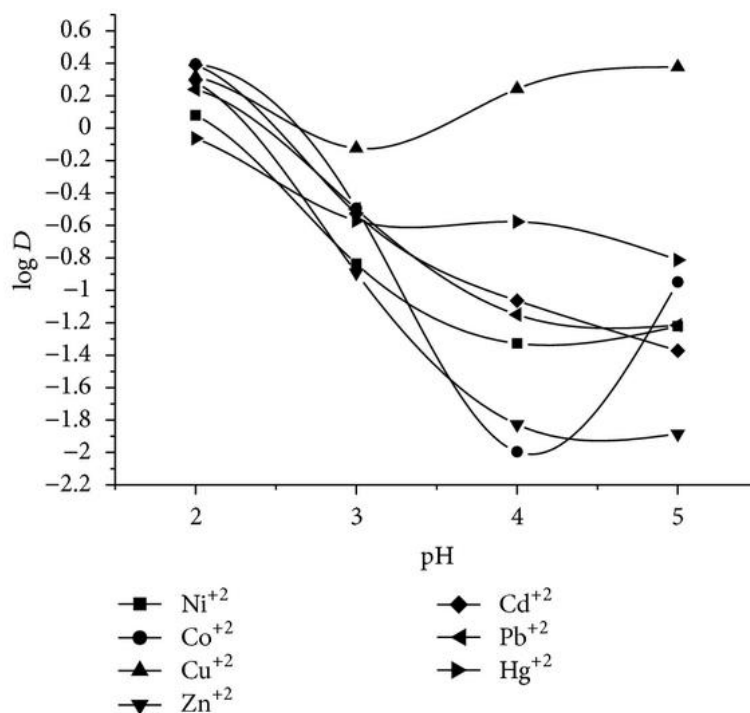
Figure 2 Ph-log *D* graph of L1 ligand.
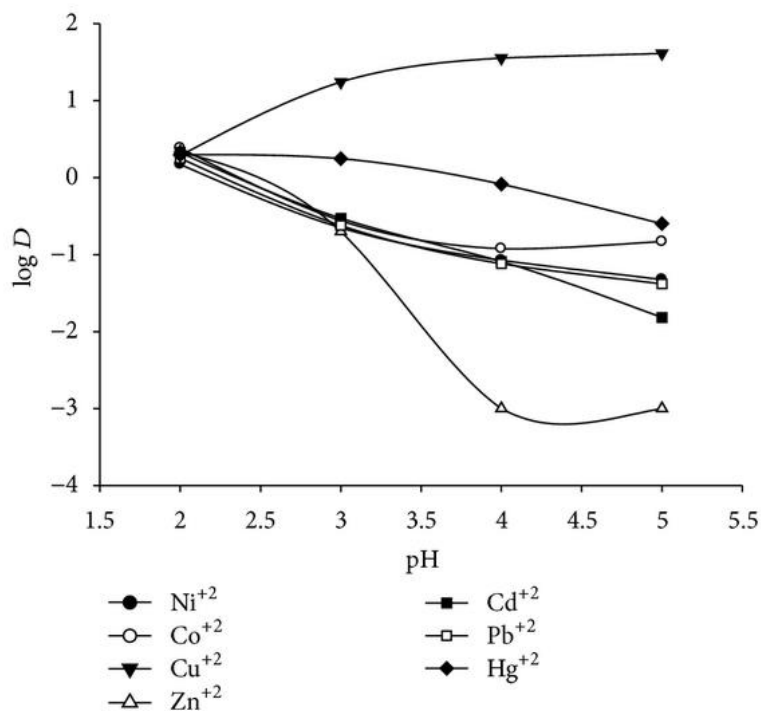
Figure 3 pH-log *D* graph of L2 ligand.

Generally, the effect of crown ethers and metals is connected not only with ion radius and cavity size but also with the position of donor atoms in ligand molecules and their numbers with the structural characteristics of the whole-molecule, conformational changes forming during the effect with metals and with **the opposite** 1.72 A^0 Cd^{2+} ion radius were very close to each other $\cong$ 1.94 A^0 mentioned factors. Among extracted metals that worked at cavity radii near **one another**, but it was observed that Cd^{2+} **wasn't** active in extraction [31]. When extraction to organic **innovate there's a rise** Cu^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} until pH$\cong$ 3. 00. When pH- log D graph of L3 until pH (Figure 4) and L4 (Figure 5) is examined the decrease of log D value of Hg^{2+} is clearly seen. For the remaining metal cations, partially increasing logarithmic curves are observed. It **is** said that for this ligand (L4) in pH 2.00–5.00 range metal extraction **are often** done.
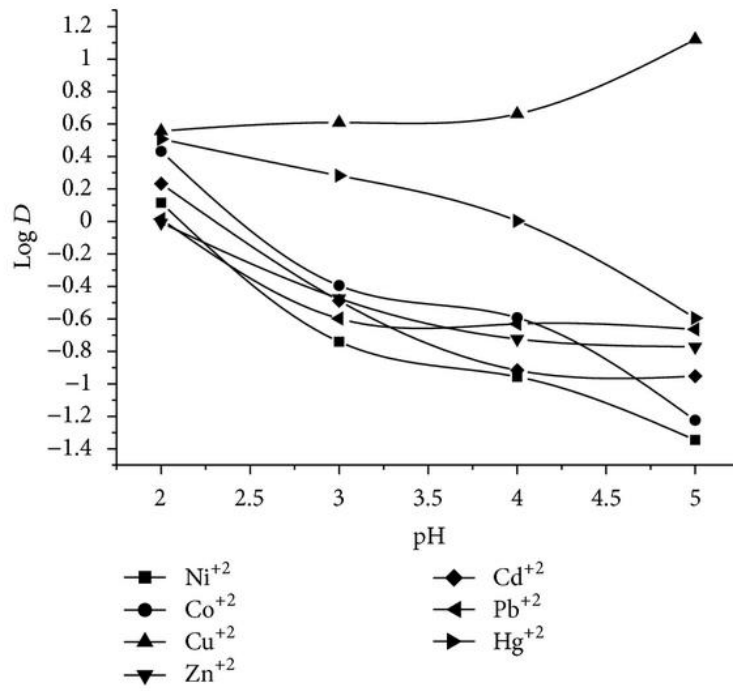
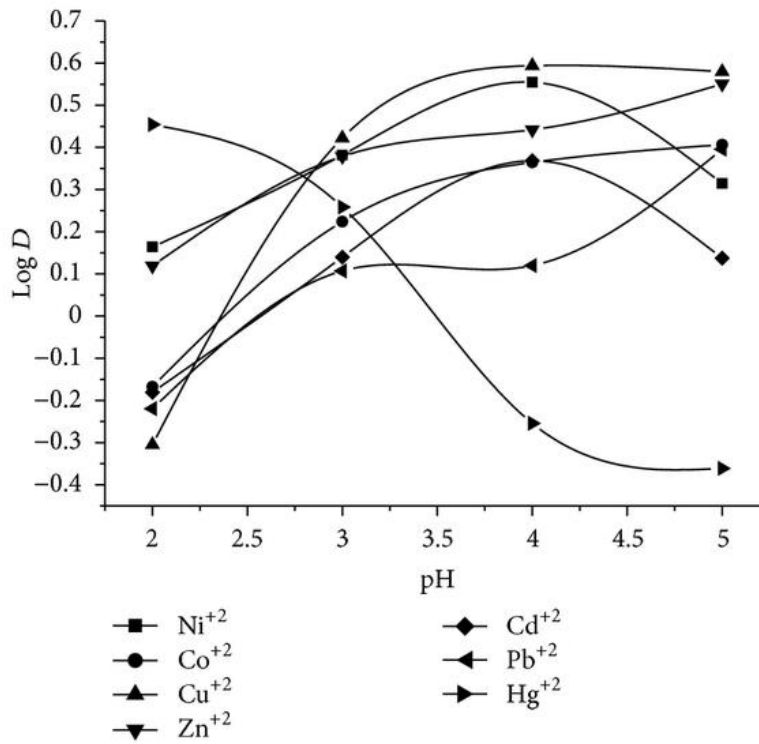Figure 4‗pH- log *D* graph of L3 ligand.

Figure 5‗pH- log *D* graph of L4 ligand.

When pH increases, distribution coefficient **should** increase too. But **because the** structure of ligands **doesn't** suit **the final** mechanism, logarithmic curves are observed. The slopes of linear parts of pH- log D graph are usually in fractional numbers. **Constant with** Zolotov et al. [32, 33], as certain parts **of those** graphs show protonation or deprotonations while descending parts show metal hydrolyses. However, **consistent with** some author all the experimentas were done to calculate pH curves **leading to** different shaped curves in each trial.

It is not correct **to elucidate** the carry of extracted metals by crown ether oxime groups to cation radius. **While** Hg^{2+} cation radius **is extremely near** Cd^{2+} radius, their extraction values are very different **the identical** case was examined by Yordanov and Roundhill who commented on crown ether and calixarene extractions [31].

Even though complex **to create** inclination of oxime groups to nickel metal is big of oxime groups to nickel metal, extraction percent is lower compared to copper. Dioxime compounds usually form N, N, or N, O chelate complexes. That complex formation **is expounded** to **the sort** of the donor atom, ligand structure, and stability of the complex, and solubility of complex is examined; **compared** to extraction data **of comparable** oximes **within the** literature [24–30, 34], **it's** seen that ligands **utilized in** our research except the commercial ones extract copper in big amounts. **It's** surprising that Hg^{2+} can also be carried when Hg^{2+} is extracted in large values at pH$\cong$ 2 as previously given extraction Table 2-5. **It had been** observed that oximes **will be utilized in** liquid-liquid extraction as they include N group. Metal-ligand ratio of all ligands is $1:1$ for Cu^{2+}. Metal-ligand ratio of oximes not having crown ether group is $1:2$ for Hg^{2+}. And metal-ligand ratio of oximes having crown ether groups for Hg2+ is $1:1$. Inoue and friends [35] have **advises** that **one among the explanations** of the observed unordinary stoichiometricals **is that the** lack of harmony of metals and cycle size. Normally as metal would coordinate with nitrogen **thanks to** oxime terminal metal: ligand ratio should be $2:1$. Here, complexes **within the** extraction and solid phases resemble **one another** especially **for his or her** characteristic structures. **The rationale** is that, in both phases, **there's** not strong solvation. The obtained extraction results of L1–L4 with the series of metal cations: alkali metals (Li^+, Na^+, K^+, and C^{s+}), transition metals (Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}), and Pb^{2+} are given in Tables 2–6. These results indicate that the compounds can be used for extraction especially of Cu2+ metal cations, which is containing this metal cation. The extractions of

selected metal cations with L2 are much before than those of other compounds. The solvent extracted Cu^{2+} and Hg^{2+} metal cations into CH2Cl2 at different concentrations of L1–L4 are shown in Figures 6 **and seven**. The obtained log D versus log L plot displayed in Figures 6 **and seven** is shown as $1:1$ in ratio of metal-ligand for Cu^{2+} with L1–L4 and for Hg^{2+} with L3, L4 and $1:2$ in ratio of metal : ligand for Hg^{2+} with L1, L2.
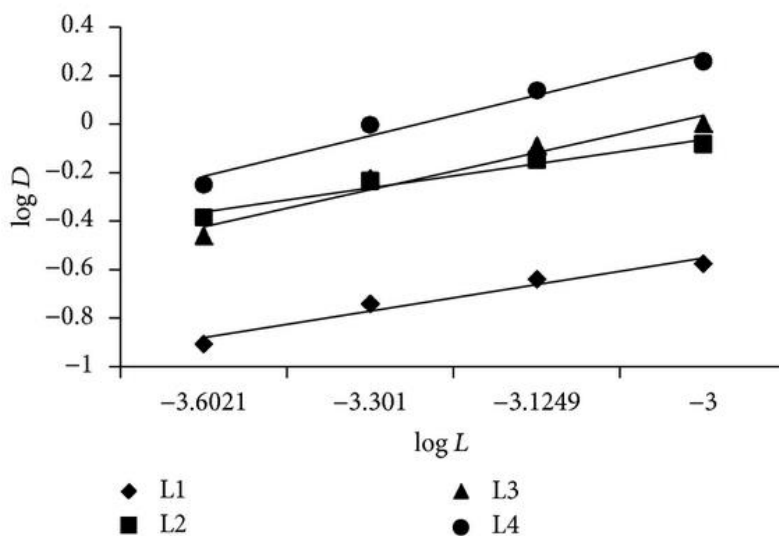

Figure 6 Plots of log *D* versus log L for Hg^{2+} of ligands.
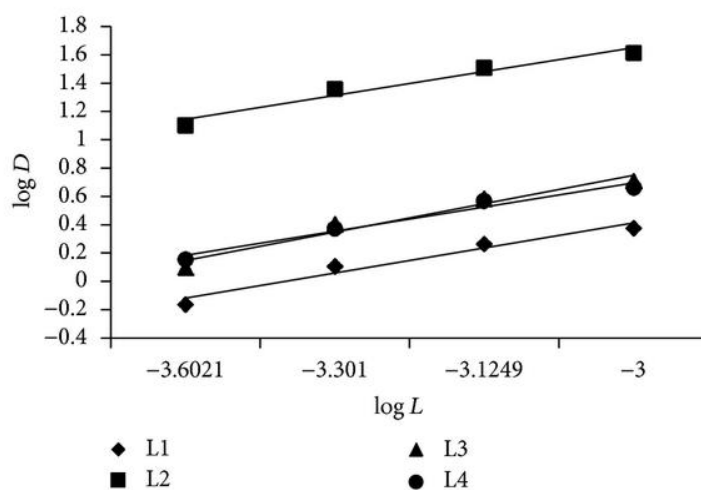

Figure 7 Plots of log *D* versus log L for Cu^{2+} of ligands.

The proposed equation is described as follows:

The proposed equation is described as follows:

$$\log D = \log K_{ex} + \log [\text{Pic}^-]^n + x \log [\text{L}]. \tag{6}$$

The slopes of curves in the extraction of Cu^{2+} and Hg^{2+} with **L1–L4** are describes later. It can therefore suggest that the ratio of metal-ligand is $1:1$ or $1:2$ due to probably zwitter ion character of ligands containing O and N atoms:

$n = +2$; M = Cu, $x = 0.896$ (L1), 0.850 (L2), 1.012 (L3), 0.852 (L4), respectively,
$n = +2$; M = Hg; $x = 0.554$ (L1), 0.502(L2), 0.773(L3), 0.838(L4), respectively.

The logarithmic extraction constant $\log K_{ex}$ (K_{ex} in mol/L) corresponding to (6) is calculated:

$Log K_{ex} = 12.27, 13.37, 12.94, 12.39$ for Cu^{2+} with L1–L4, respectively,
$Log K_{ex} = 10.29, 10.62, 11.53, 11.97$ for Hg^{2+} with L1–L4, respectively.

Since IA group cations are at hard characteristic, **per** hard-soft acid-base rule, hard metals react with hard donor group and soft metals react with soft donor groups. So, extraction characteristics against alkali metals of oximes having and not having crown ethers were examined.

Oxime derivatives of crown ether (L3-L4) are very effective in transferring the **alkaline metal** cations. Crown ether groups having ligands carry all alkali metals from aqueous phase to organic phase, but especially Na^+ cation is carried clearly. As seen in Table 6 and Figure 8, **this is often thanks to** the appropriateness of the ion diameter of Na^+ ion and cavity of crown ether cycle. Cavity diameter of crown ether cycle is $1.72\ A^0$–$1.54\ A^0$, and ion radius of sodium ion is R : $1.90\ \text{Å}$.
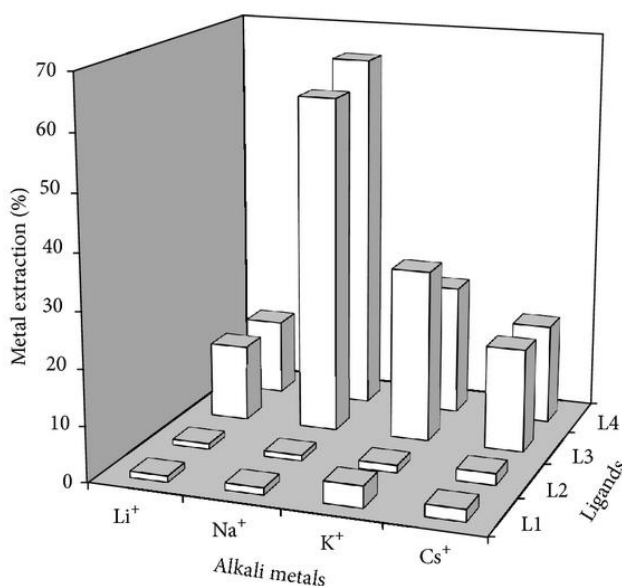

Figure 8 Extraction of alkali metal cations with ligands.

The previously mentioned phenomena will be explained by the (hard-soft) acid-base principle as follows: C=N–OH could be a soft base and hence has stronger affinity towards soft basic metal cations than hard metal cations. The strong participation of the N-OH group in complex formation was further confirmed by the results shown for extraction experiments with ligands.

The results of solvent extraction of metal picrates from aqueous phase to dichloromethane phase with oxime derivatives of crown ether are summarized in Table 6. It's known that 15 membered all-oxygen crown ethers have high selectivity for Na^+ ion. L3 and L4 shows approximately similar extractability against the opposite metallic element cations (Li^+, K^+, and Cs^+) and shows no selectivity for these cations when pH is 7.0. A selectivity becomes apparent as within the order $Na^+ > K^+ > Cs^+ > Li^+$.

Previous investigations on solvent extraction of metallic element cations from aqueous phase into organic solvents with all-oxygen crown ethers like 12-crown-4, 15-crown-5 and 18-crown-6 indicate that the subsequent orders are common trends $Li^+ \gg Na^+ > K^+ > Rb^+ > Cs^+ >$, $Na^+ \gg K^+ > Rb^+ > Cs^+ > Li^+$, and $K^+ \gg Rb^+ > Cs^+ > Na^+ > Li^+$, respectively. These orders are explained in terms of the link between the crystal radius of metal ions and also the size of crown ethers [36, 37]. In our metallic element extraction experiments for oxime compounds having the identical crown ether group, $Na^+ > K^+ > Cs^+ > Li^+$ activity order was observed. And this can be in favour of the literature.

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