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DETERMINATION OF THE STOICHIOMETRIES OF THE NICKEL COMPLEXES WITH CARBOXYLIC ACIDS BY EXTRACTION

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ABSTRACT

In this study the extraction of nickel, from aqueous $NiCl_2$ and $NiSO_4$ solutions with octanoic, decanoic and lauric acid dissolved in kerosen was investigated within the pH range of 6–8. The probable compositions of the complex structure was determined by statistical method.

The calculations suggest that with 0.5 M octanoic acid, 0.5 and 1 M decanoic acid dimeric complexes are formed. The number of solvating acid molecules per metal ion 0,1 or 2.

With 1 M octanoic acid it forms monomeric and dimeric complexes. The number of solvating acid molecules per metal ion is found to be 0,1 or 2.

Monomeric complexes are formed with 0.5 M lauric acid. The number of solvating acid molecules per metal ion is 0 or 1.

INTRODUCTION

The main subject of our study which was printed in "DOĞA" (Gündüz, 1984) was to investigate the utilization of fatty acids in the extraction processes of nickel, and to research various conditions which effect to reach the maximum extraction yield. At the result of this study, maximum extraction yields at 25°C, pH's are between 7.8 and 8.0, and after agitation for one hour, were reached as indicated below:

a) 80–83 %, by octanoic acid

b) 97–98 %, by decanoic acid

c) 99 %, by lauric acid.

Applicability of these three fatty acids to industrial processes was researched by using Southerneast Anatolia asphaltites which are known as containing remarkable amount of nickel. The yield of nickel extraction from leaching solution of asphaltite ash was fixed as 67 %.

In this study, it's aimed to determine the structure of complex salts which are formed by above-mentioned fatty acids and nickel in the organic phase by statistical method.

In order to calculate the structure of the complex salt; some researchers (Fletcher, 1964; Shikheeva, 1965; Kojima, 1970; Tanaka, 1967) are used pH versus logD curves which are derived from various acidic extractant and metal concentrations.

Jaycock and Jones (1967) have derived another method by using only one pH versus logD curve. Both methods are observed to be valid for the conditions of 10^{-3} M or lower metal concentrations. The statistical method which is developed by Van der Zeeuw (1979) can be applicable to the metal concentrations higher than 10^{-3} M. From this point of wiev, we've tried to identify the structure of complex salts by the istatistical method.

A.J. Van der Zeeuw studied the recovery of metal ions from their aqueous solutions to organic phases by using acidic extractants and derived a statistical method to determine the structures of the complexes formed. In this method one makes use of the distribution coefficients (Distribution coefficient is the ratio of the metal concentration in organic phase, to the concentration in aqueous phase) $D = \frac{[M]org}{[M]aq}$, the pH values at which extraction is carried out. According to this method if these "D" values are plotted against the pH in ideal conditions one is supposed to obtain a linear line with a slope equal to the number of extracting groups bound to metal through covalent bond. This ideal state is seldom achieved due to various reasons. One of the reasons is that the ionic strength and the activities of the species formed in organic phase do not remain constant during extraction. The other reason may be the complications which arise from the hydrolysis of the metal ions and the polymerisation of metal complexes in aqueous solutions.

Despite some theoretical disadvartages, this method is widely employed in practice. Because only one logD / pH curve suffices to give satisfactory results.

COMPUTER (STATISTICAL) METHOD

The extraction of metal ions in aqueous phase by acidic extractants can generally be written as (*);

$$M_{(aq)} + \frac{n+m}{p}(HA)_{p,org} \leftrightarrow \frac{1}{x}(MA_n.mHA)_x + nH_{aq} \quad (1)$$

The equilibrium constant of this reaction can be defined as;

$$K' \frac{[C]_{org}^{1/x}[H]_{aq}}{[M]_{aq}\left[(HA)_p\right]_{org}^{\frac{n+m}{p}}} \cdot \frac{\gamma_{C,org}^{1/x}\gamma_{H,aq}^{n}}{\gamma_{M,aq}\gamma_{(HA)_{p,org}}^{\frac{n+m}{p}}} K.B \quad (2)$$

where $[C] = (MA_n.mHA)_x$

The results of the measurements generally give the values of the analytical distribution coefficient D, defined as;

$$D = [M]_{org} / [M]_{aq} \quad (3)$$

$$[C]_{org}^{1/x} = \left[\frac{1}{x}M\right]^{1/x}[M]_{org}^{1/x}\left(\frac{1}{x}\right)^{1/x} = [M]_{org}[M]_{org}^{\frac{1-x}{x}}\left(\frac{1}{x}\right)^{1/x}$$

From (3)

$[M]_{org} = D\ [M]_{aq}$, and therefore

$$[C]_{org}^{1/x} = D.\ [M]_{aq}\ [M]_{org}^{\frac{1-x}{x}}\left(\frac{1}{x}\right)^{1/x} \quad (4)$$

Substitution of (4) into (2) gives,

$$K' = \frac{\left\{D\ [M]_{org}^{\frac{1-x}{x}}\left(\frac{1}{x}\right)^{1/x}\right\}[H]_{aq}}{\left[[(HA)]_p\right]^{\frac{n+m}{p}}} . B$$

If we take the logarithms,

$$\log D = \log K' - \log B + \{(x-1)/x\}\ \log[M]_{org}$$

$$+ \frac{1}{x}\log x + npH + \left\{\frac{(n+m)}{p}\right\}\log (HA)_p \quad (5)$$

One may further write:

$$[HA]_o = [HA]_{org} + [HA]_{aq} + [A]_{aq} + (n+m)\ [M]_{org}$$

Since the solubility of HA and the complex in the aqueous phase is low, $[A]_{aq}$ and $[HA]_{aq}$ can be neglected. Therefore,

$$[HA]_o = [HA]_{org} + (n + m)\ [M]_{org} \quad \text{or,}$$

$$[HA]_{org} = [HA]_o - (n + m)\ [M]_{org}$$

If this value is substituted into (5) one obtains,

$$\log D = \log K' - \log B + \{(x - 1)/x\} \log [M]_{org} + \left(\frac{1}{x}\right) \cdot \log x + npH + \frac{n + m}{p} \log \left\{ \frac{[HA]_o - (n + m)\ [M]_{org}}{p} \right\}$$

$$\log K = \log D - \{(x - 1)/x\} \log [M]_{org} - \left(\frac{1}{x}\right) \log x - npH - \frac{n + m}{p} \log \left(\frac{[HA]_o}{p} - \frac{n + m}{p}\ [M]_{org}\right)$$

(*) Nomenclature

M : metal ion

HA : acidic extractant

A : anion of extractant

B : activity coefficient of product

$[HA]_o$: initial extractant concentration

$\gamma_{a,b}$: activity coefficient for the species a in phase b

P : degree of polymerization of the extractant in diluent (In this experiment has been taken to be 2.It is known from the literature that carboxylic acids in various non–aqueous apolar solvent are dimeric)

n : number of extractant groups bound to M in a "salt like" manner

m : number of extractant molecules bound as solvation molecules

x : degree of polymerization of the extracted complex

c : extracted complex

K : equilibrium constant with respect to concentrations

K′ : equilibrium constant with respect to activities

In this method n, m and x are given 0, 1, 2 values and

a) log K and mean log $\overline{K}$ values are determined for each experiment,

b) The slope of the most suitable line obtained for pH vs log K plot

$$\text{Slope } \beta 1 = \frac{\Sigma\ (pH - \overline{pH})\ (\log\ K - \log\overline{K}))}{\Sigma\ (\overline{pH} - pH)^2}$$

$$b^* = \log\ \overline{K} - \beta 1\ \overline{pH}$$

$$\log\ \hat{K} = \beta 1\ pH + b^*$$

$\log\ K - \log\ \hat{K}$ are determined

$$\sigma^2 = \frac{\Sigma\ (\log\ K - \log\ \hat{K})^2}{n - 2} \qquad n = \text{number of experiments.}$$

$$S^2\ \beta 1 = \frac{\sigma^2}{\Sigma\ (pH - \overline{pH})^2}$$

"$t_{calculated}$" value known as student'st is found from the following equation

$$t_{calculated} = \frac{\beta 1}{S\beta 1}$$

These $t_{calculated}$ values are compared with those "$t_{critical}$" values obtained from the "t" table. The n, m, x values corresponding to $t_{calculated} \leq t_{critical}$ give the possible structures.

EXPERIMENTAL

The nickel solutions to be extracted were prepared in 0.02 M concentration from $NiCl_2.6H_2O$ and $NiSO_2.6H_2O$. The pH adjustments were carried out with NaOH, HCl and H_2SO_4. The pH values were read by a Beckman pH meter. Then 0.5 and 1 M octanoic, 0.5 and 1 M decanoic and 0.5 M lauric acid solutions were prepared in kerosene. 20 ml of nickel solutions were taken and pH adjustments were made. They were put in 100 ml flasks with a 20 ml fatty acid solutions. The extraction procedures were carried out at a pH range of 6–8 and $25 \pm 1°C$ in a water bath by constant shaking for about an hour. The extracted mixtures were kept in seperatory funnel for 1 hour in order to facilitate phase seperation. The water phase was seperated. 1 ml of this phase was taken and diluted to 100 ml for the determination of concentrations. The concentration were determined by Varian–Techtron–1200 model atomic absorption spectrophotometer.

EXPERIMENTAL RESULTS

Extraction of 0.5 M Octanoic acid–0.0203 M $NiCl_2$

Experiment no	pH	Metal conc. (Org) mol/lt	Metal conc. (inorg) mol/lt	logD
1	7.5	0.0007	0.0196	–1.4472
2	7.8	0.0044	0.0159	–0.5580
3	8	0.0105	0.0098	0.0300
4	8.2	0.0162	0.0041	0.5967
$t_{critical}$ = 4.30				

No	n	m	x	log $\bar{K}$	β_1	t_{cal}
1	1	0	1	– 7.9126	1.9398	$6.89.10^1$
2	2	0	1	–15.4784	0.9752	$5.89.10^1$
3	1	1	1	– 7.6034	1.9656	$1.19.10^2$
4	2	1	1	–15.1593	1.0168	$5.91.10^1$
5	1	2	1	– 7.2843	2.0172	$2.81.10^2$
6	2	2	1	–14.8323	1.0913	$7.2..10^1$
7	1	0	2	– 6.9055	0.9424	7.98
8	2	0	2	–14.4688	–0.0273	$*2.15.10^{-1}$
9	1	1	2	– 6.5938	0.9731	7.66
10	2	1	2	–14.1497	0.0236	$*6.84.10^{-1}$
11	1	2	2	– 6.2747	1.0247	9.72
12	2	2	2	–13.8228	0.1578	$*6.74.10^{-1}$

Possible structures $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$

(The n, m, x values corresponding to * give possible structures)

Extraction of 1M Octanoic acid–0.0203 M $NiCl_2$

Experiment no	pH	Metal conc. (Org) mol/lt	Metal conc. (inorg) mol/lt	logD
1	7.4	0.0018	0.0185	–1.0095
2	7.6	0.0070	0.0133	–0.2754
3	7.8	0.0151	0.0052	0.4714
4	8	0.0169	0.0034	0.7093
$t_{critical}$ = 4.30				

No	n	m	x	log $\bar{K}$	β_1	t_{cal}
1	1	0	1	– 7.5733	1.9578	10.39
2	2	0	1	–15.1160	0.9755	*2.2337
3	1	1	1	– 7.4160	1.9755	4.5216
4	2	1	1	–14.9542	1.0054	*2.27
5	1	2	1	– 7.2542	2.0059	4.549
6	2	2	1	–14.7875	1.048	*2.345
7	1	0	2	– 6.622	1.1445	4.508
8	2	0	2	–14.2049	0.162	*0.630
9	1	1	2	– 6.5049	1.162	4.52
10	2	1	2	–14.0430	0.193	*0.739
11	1	2	2	– 6.3430	1.1925	4.587
12	2	2	2	–13.8764	0.2339	*1.18

Possible structures $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$

Extraction of 0.5 M Decanoic acid–0.0202 M $NiSO_4$

Experiment no	pH	Metal conc. (org) mol/lt	Metal conc. (inorg) mol/lt	logD
1	7.7	0.0021	0.0181	–0.9355
2	7.8	0.0065	0.0137	–0.3238
3	7.9	0.0133	0.0066	0.3043
4	8	0.0194	0.0008	1.3847
$t_{critical}$ = 4.30				

No	n	m	x	log $\bar{K}$	β_1	t_{cal}
1	1	0	1	– 7.4371	6.616	8.238
2	2	0	1	–14.9721	5.696	7.063
3	1	1	1	– 7.1221	6.969	8.3025
4	2	1	1	– 1.6484	5.84	7.2
5	1	2	1	– 6.7984	6.84	8.4
6	2	2	1	–14.3622	6.24	5.7
7	1	0	2	– 6.5309	5.012	4.969
8	2	0	2	– 1.0659	4.09	*3.908
9	1	1	2	– 6.2159	5.092	4.868
10	2	1	2	–13.7423	4.236	*4.0038
11	1	2	2	– 5.8923	5.2349	4.9465
12	2	2	2	–13.406	4.4287	*4.16

Possible structures $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$

Extraction of 1 M Decanoic acid–0.0202 M $NiSO_4$

Experiment no	pH	Metal conc. (org) mol/lt	Metal conc. (inorg) mol/lt	logD
1	7.7	0.0060	0.0142	–0.3741
2	7.8	0.103	0.0099	0.0172
3	7.9	0.0161	0.0041	0.5940
4	8	0.0199	0.0003	0.8210
$t_{critical}$ = 4.30				

No	n	m	x	log $\bar{K}$	β_1	t_{cal}
1	1	0	1	– 7.4319	3.176	6.965
2	2	0	1	–15.1227	2.208	4.795
3	1	1	1	– 7.2727	3.208	6.97
4	2	1	1	–14.9578	2.26	4.87
5	1	2	1	– 7.1078	3.26	7.01
6	2	2	1	–14.7866	2.336	4.991
7	1	0	2	– 6.6197	2.295	5.93
8	2	0	2	–14.5339	1.33	*3.47
9	1	1	2	– 6.4603	2.330	6.019
10	2	1	2	–14.1452	1.384	*3.55
11	1	2	2	– 6.2952	2.284	6.114
12	2	2	2	–13.9739	1.462	*3.70

Possible structures $(NiA_2)_2$, $(NiA_2HA)_2$, $(NiA_22HA)_2$

Extraction of 0.5 M Lauric acid–0.0203 M $NiCl_2$

Experiment no	pH	Metal conc. (Org) mol/lt	Metal conc. (inorg) mol/lt	logD
1	7.6	0.0011	0.0192	–1.2419
2	7.7	0.0086	0.0117	–0.1337
3	7.9	0.0171	0.0032	0.7279
4	8	0.0195	0.0008	1.3869
$t_{critical} = 4.30$				

No	n	m	x	log $\bar{K}$	β_1	t_{cal}
1	1	0	1	– 7.3091	5.14	6.299
2	2	0	1	–14.7924	6.2012	*4.1109
3	1	1	1	– 6.9924	5.202	6.342
4	2	1	1	–14.4645	4.3092	*4.1899
5	1	2	1	– 6.6645	5.309	6.3964
6	2	2	1	–14.1249	4.4639	5.3002
7	1	0	2	– 6.3635	3.6076	5.744
8	2	0	2	–13.8802	2.8036	6.76
9	1	1	2	– 6.0802	3.804	9.190
10	2	1	2	–13.5524	2.911	7.27
11	1	2	2	– 5.7524	3.911	9.36
12	2	2	2	–13.2127	3.067	7.26

Possible structures NiA_2, NiA_2HA.

ÖZET

Bu çalışmada kerosende çözünmüş oktanoik, dekanoik ve laurik asit kullanılarak $NiCl_2$ ve $NiSO_4$'ın sulu çözeltilerinden nikel ekstraksiyonu yapıldı ve pH 6–8 arasında değişimi incelendi. Organik fazdaki kompleks yapının muhtemel bileşimleri istatiksel hesap yöntemi ile tayin edildi.

Bu sonuçlara göre 0,5 M oktanoik asit, 0,5 M ve 1 M dekanoik asit ile dimerik komplekslerin oluştuğu belirlendi. Solvatize asit molekül sayısı 0,1 ve 2 olarak tesbit edildi.

1 M oktanoik asit ile monomerik ve dimerik yapılar oluştuğu sonucuna varıldı. Solvatize asit molekül sayısı 0,1 ve 2 olarak tayin edildi.

Laurik asit ile ise monomerik komplekslerin oluştuğu bulundu. Solvatize asit molekül sayısı 0 ve 1 olarak tesbit edildi.

REFERENCES

FLETCHER, A.W. and FLETT, D.S., 1964. *J. Appl. Chem.*, 14, 250.

GÜNDÜZ. N., SÖKMEN, N., 1984. Doğa Bilim Dergisi, Seri B, Cilt B, Sayı 1.

JAYCOCK, M.J. and JONES, A.D., *Solvent Extraction Chemistry*, *Proc. Int. Conf. Gothenburg*, 1966, North - Holland, Amsterdam, 1967, p.1.

KOJIMA, I., UCHIDA, M. and TANAKA. M., 1970. *J. Inorg. Nucl. Chem.*, 32, 1333.

SHIKHEEVA, L.V., 1965. *J. Inorg. Chem. USSR* (Engl. Transl.) 10, 808.

TANAKA, M., NAKUSAKA, N. and GOTO, S., in - D. DYRSSEN et. al. (Editors), *Solvent Extraction Chemistry*, *Proc. Int. Conf. Gothenburg*, 1966, North–Holland, Amsterdam, 1967, p. 154.

VAN der ZEEUW, A.J., 1979. *Hydrometallurgy*, 4, 21–50.