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PH Effect on Sodium Thiocyanate(NaSCN)Alkali Salt Liquidate-liquid Extraction and Thiocyanate of potassium (KSCN) by Neuter and Anionic Extractants

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ABSTRACT: The liquidate-liquid extraction is an efficient method for the treatment, the separation of the metallic ions of the industrial worn-out waters, in which the concentrations made of metal can be important. This method is based on the possibility of transferred one or several solution contained in an aqueous phase toward a non-miscible organic phase by contact between the two phases. The present work is about the extraction of the sodium thiocyanate and the thiocyanate of potassium (NaSCN and KSCN) by the benzo 15 crown 5 (B15C5), the dicyclohexyl 18 crown 6 (DC18C6), aliquat 336 and the sorting-octyl-phosphine (TOPO) in the toluene and the mixture toluene / acetone. The concentrations in alkali ions transferred in the organic phase according to the pH of the aqueous phase have determined summers. The analysis of the results gotten show that with the DC18C6 and B15C5 the extraction takes place in domains of strong basicity with a weak extraction rate. Otherwise the aliquat 336 gives a rate of extraction of 94, 32% to pH=6, 57. Different parameter to know the volume of the organic phase and the time of agitation has been studied in order to optimize the efficiency of extraction. The extracted metals are analyzed by UV-Visible spectrométrie.

KEY WORDS: Liquid-liquid extraction, alkaline salts, agent extractant, stoichiometry, benzo 15 couronne, toluene

I. INTRODUCTION

Proceeded used in hydro metallurgy for the separation, the recuperation and the exploitation of the rare chemicals, the liquidate-liquid extraction consists to make pass a substance that interests us of a solvent, of which she/it is often difficult to separate, to another (named solvent of extraction), of which she/it will be easily isolable. This operation, usually achieved by agitation, is possible provided that the two solvents are very little or not miscible between them. In the industry, the liquidate-liquid extraction competes the other processes, as the distillation, crystallization, the adsorption... etc. In some cases it imposes herself/itself in an indisputable manner, notably when the technological or physico-chemical conditions are favorable to him, as it is the case for:

The separation of constituent to neighboring boiling points (separation of some aromatic hydrocarbons and aliphatiques).

- The separation azéotrope
- The separation of compounds thermosensibles or unsteady (antibiotics)
- The concentration and the purification of dilute solutions, operation often more economic than the distillation [1,2,3,4,5,].

To achieve by means of the molecules the mechanisms of extraction differs according to the chemical nature of the agent extractant and the interactions generated at the time of the transfer of the solution of a phase to another. One distinguishes 3 fashions of extractions conventionally [4,6,7]:

- extraction by solvation;

- extraction by exchange of pressed;
- extraction by exchange of anions.

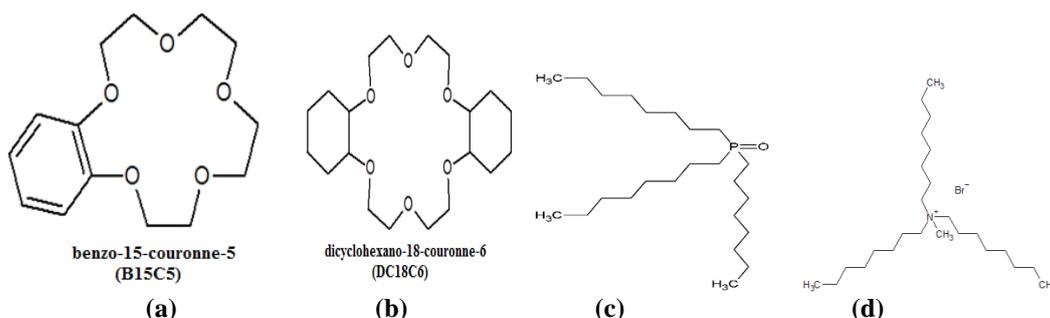
The DC18C6 and B15C5 are compounds macrocyclics of the family of the ethers crown catalog as extractants solvant. Indeed through the intermediary of their groupings donors who are the atoms of oxygens, these compounds can substitute themselves for the molecules of hydration of the metallic cation and solvater on his/her/its turn metal. This last is extracted as a pair of ions solvatée. Several studies showed that the extraction of pressed them by ethers crown depends of the parameter to know the PH, of the nature of the mineral anion, of the agitation time [7, 8,9] etc..... The objective of this work is to study the performances of the different parameter at the time of the extraction of NaSCN and KSCN by the B15C5, DC18C6, TOPO and ALIQUAT while making vary the nature of the diluents (toluène, toluène/acétone, diethyle ethers, diethle éthers/acétone, tetrachloromethane).

II. MATERIAL AND METHODS

A. MATERIAL

1. The mineral salts and the organic products

- The thiocyanate of NaSCN sodium and the thiocyanate of KSCN potassium of purity superior to 97% are provided by guanghua sci.co.ltd chemical;
- the chloride of iron hexahydraté (FeCl₃, 6H₂O) of purity (99%) is provided by guanghua sci.co.ltd chemical;
- the nitric acid (HNO₃) of purity (52,5%) is provided by Fisher Chemical;
- the Benzo 15 Crown 5(B15C5) (fig1 has) of purity superior to 97% is a mixture of isomers (cis-syn-cis and cis-anti-cis) well stocked by Fluka;
- the Dicyclohexyl 18 Crown 6 (DC18C6) (b fig1) of molar mass 372, 51 g.mol⁻¹, of purity superior to 97% is a mixture of isomers (cis-syn-cis and cis-anti-cis) is provided by Fluka;
- The oxide of Sorting-Octyl-Phosphine (TOPO), Fig.1. (c) is an agent extractant solvant or neutral, of mass molar 385,64 g.mol⁻¹, of purity superior to 99% and is provided by Merck;
- The Bromide of N-méthyl-N,N-dioctyl-1-octanaminium (C₂₅H₅₄BrN) or Aliquat 336 Fig.1.(bs) well stocked by Molekula.



Face 1: structure of the extractants

The toluène and diethyl ethers are provided by Prolabo and are washed several times to water distilled to eliminate the stabilizing agents.

2. The devices

- A spectrophotometer monochromatic MODEL 4101.La length of wave is fixed to 456 nm.
- An electronic analytic Balance of mark Specified 205 A.

B. METHODS

1. Preparation of the solutions

The solution colorimétrique is prepared in a vial of 1L; by dissolution of 5,4058 g of FeCl₃, 6H₂O in 18,116 ml of acid nitric HNO₃ (52,5%) then one completed with water distilled until the feature of tonnage. This solution allowed us to prepare the solutions stallions.

2. liquidate-liquid extraction

The operations of liquidate-liquid extraction have been made in a bulb to decant 100 ml to the ambient temperature. 20 ml of aqueous phase and 20 ml of organic phase have been put in contact and one agitates mechanically and energizing in the goal to increase the surface of contact and to optimize the diffusion of the solution between the two phases. The agitation lasted 30 minutes, time judged necessary for the realization of the balance of the extraction. This stage constitutes the extraction. After the agitation, a volume known of the organic phase is appropriated and put in contact with water distilled to assure the against extraction. In end the two separated phases, we appropriated 5 ml of the aqueous phase that we place then in a vial of 50 ml we complete with the solution colorimétrique. The studied metals are analyzed by spectrophotometry. All experiences have been repeated three times in order to ascertain the reproducibility of the results.

III. RESULTS AND DISCUSSION

A. CHOICES OF THE DILUENT

In the setting of this experimentation, we also studied the extraction of the two salts the NaSCN and the KSCN to 10-3M by the B15C5 to 10-3M in the different diluents. Arbitrarily a neutral pH has been chosen to achieve these tests. The analysis of the complex has been done by dosage with a solution colorimétrique. The results of this analysis give us concentrations average of the organic phase of [NaSCN] org and [KSCN] org. These results allow us to calculate the coefficients of distribution. The I picture gives us the different values of the distribution coefficient gotten according to the diluents.

I picture: coefficient of distribution of salts with B15C5

Extractant Diluents	B15C5	
	$D = \frac{[NaSCN]_{org}}{[NaSCN]_{aq}}$	$D = \frac{[KSCN]_{org}}{[KSCN]_{aq}}$
toluene	0,058	0,015
Toluène/acétone	0,205	0,185
Ether diethylique	0,072	0,051
Ether diethylique/acétone	0,09	0,088

According to these results, one sees that biggest coefficient of distribution is gotten with the mixture toluene/acetone, it would be able to explain himself by the capacity of toluene to be different comfortably after contact with the aqueous phase. On the other hand the weak rates gotten with the etherdiethylique could be due to the weak density in relation to water and in the same way this last is very volatile. These results are in agreement with the works of BOYD and LARSON that demonstrated that the proportions toluene acetone is the important parameters intervening in the extraction [10, 11, and 12]. On the other hand the coefficient of ion sodium distribution is bigger than the one of ion potassium what brings us to say that the B15C5 seems to extract ion sodium better that ion potassium.

So thereafter we also conducted the extraction of the two salts the NaSCN and the KSCN to 10-3M by the DC18C6 to 10-3M in the toluène and the mixture toluène/acétone. The results of this analysis give us a middle concentration of the organic phase of [NaSCN] org =2,01 10-4M and [KSCN] org =1,85 10-4M. The II picture gives us the different values of the distribution coefficient gotten according to the diluents.

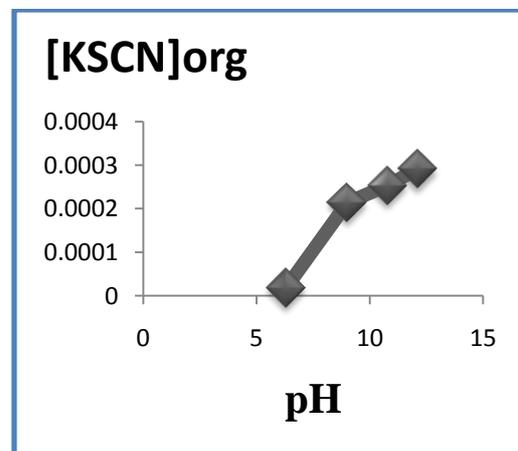
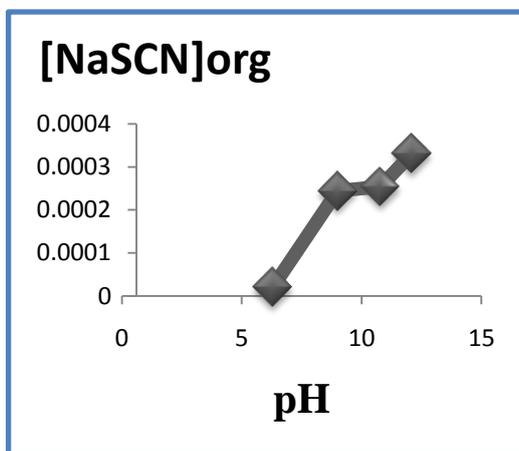
II picture: coefficient of distribution of salts with DC18C6

Extractant Diluent	DC18C6	
	$D = \frac{[NaSCN]_{org}}{[NaSCN]_{aq}}$	$D = \frac{[KSCN]_{org}}{[KSCN]_{aq}}$
Toluène	0,021	0,018
Toluène/acétone	0,201	0,190

Since the extraction of the two pressed do in the same conditions with the same against ions, the difference of the extraction rate gotten cannot be explained by the effect against ion. This difference could be explained by the size of the cavity of the two extractants The DC18C6 although of bigger cavity than the one of the B15C5 gives coefficients of distribution raised with sodium that with potassium. Some recent works showed that the B15C5 is susceptible of formed a structure 2: 1 named structure sandwich with sodium and a structure of type 1: 1 with potassium [12,13].

B. Influence du pH

The pH effects on the extraction of alkaline Na+ et K+ ions have been studied with a metal concentration equal to 0,001M in aqueous phase and by taking an organic phase containing a 0,001M concentration of extractant agent, the B15C5 and the DC18C6. The pH variation is ensured with the addition of bases corresponding to the metal. The picture 3 and 4 illustrate the variation of the metal concentration in the organic phase according to the pH.



Face N°3 Evolution [NaSCN]org according to the pH **Face 4:** Evolution of [KSCN]org according to the pH.

He/it is evident from these results that the extraction of the NaSCNs and KSCN is function of the pH of the aqueous phase, more the pH of the aqueous phase increases the concentration of metal more in the organic phase increases; it is due to the fact that when the pH increases, the free electronic doublet that the atom of oxygen possesses in the ethers crowns is more available, what permits the formation of the link ethers-crown metal.

C. EXTRACTION WITH TOPO AND ALIQUAT 336

In the goal to study the extraction of the NaSCN and KSCN with the extractants anioniques the TOPO and aliquat 336 we proceeded the following manner: the extractant to 0,001M has been dissolved in the toluene to have the organic phase and salts also to 0,001M have been dissolved in water to have the aqueous phase. . The results of this analysis give us a middle concentration of the organic phase of [NaSCN] org =0.94 10-4 M and [KSCN] org = 0.83 10-4 M with coefficients of distribution regrouped in the III picture.

III picture: coefficient of distribution according to the extractants

	TOPO	ALIQUAT
$D = \frac{[NaSCN]_{org}}{[NaSCN]_{aq}}$	0,24	0,94
$D = \frac{[KSCN]_{org}}{[KSCN]_{aq}}$	0,32	0,83

The best output of extraction 94, 3% is gotten with aliquat, extractant anionique. It is due to the capacity of this last to complex pressed them because of the presence of anion (Br -) in the molecule. On the other hand the TOPO being a neutral extractant, he/it has the same fashion of extraction that the ethers crown in relation to the aliquat that is an extractant anionique.

3.4 effect time of agitation

For the survey of this parameter, we proceeded from the following manner; the extractant to 0,001M is dissolved in the toluene, salt to 0,001M is dissolved in water the mixture has been put then under agitation during 5min, 10min and 15min. the results are regrouped below in the picture.

IV picture: Efficiency of extraction of the NaSCN according to the time of agitation

Aliquat	NaSCN		
	5min	10min	15min
Time of agitation			
$[NaSCN]_{org}^{-4}$	0,36.10 ⁻⁴ M	0,797.10 ⁻⁴ M	0,94.10⁻⁴ M
D	0,336	0,797	0,94
E (%)	33,6	79,7	94,32

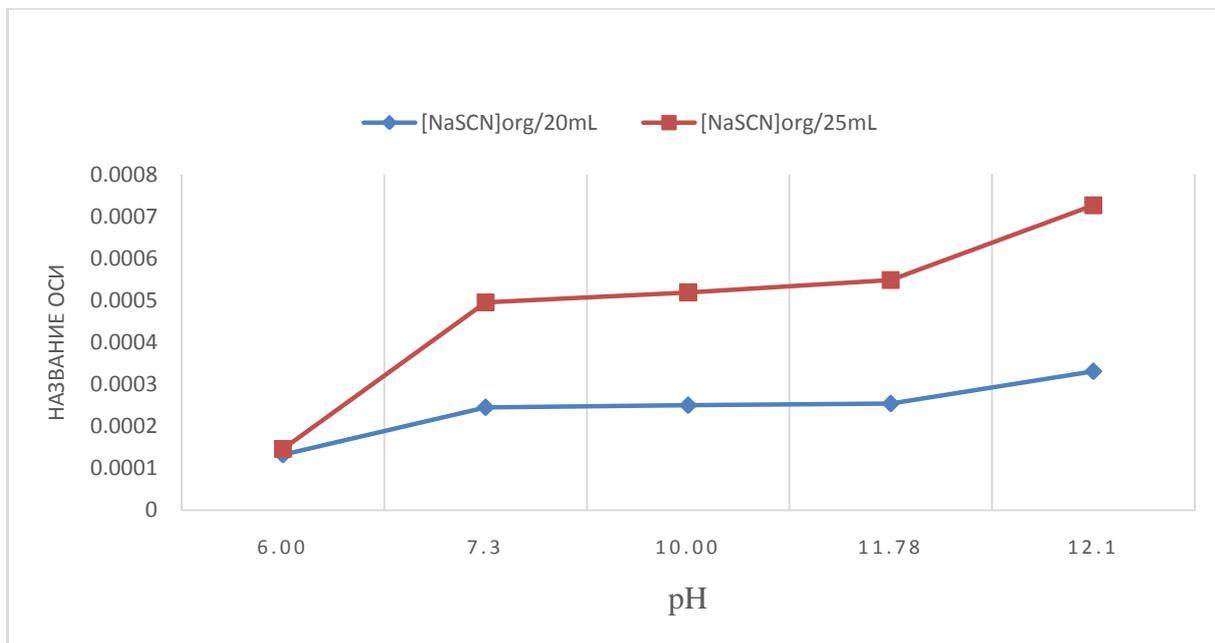
V picture: Efficiency of extraction of the KSCN according to the time of agitation

Aliquat	KSCN		
	5min	10min	15min
Time of agitation			
$[KSCN]_{org}^{-4}$	0,436.10 ⁻⁴ M	0,697.10 ⁻⁴ M	0,83.10⁻⁴ M
D	0,436	0,697	0,83
E (%)	43,6	69,7	83,33

One observes results gotten in the picture that the time of agitation is an important parameter for extraction, with the NaSCN and KSCN in the aqueous phase and the aliquat in the organic phase the output of extraction to 5min is indeed respectively of 43,6% and 33,6% and pass to 83,33% and 94,32% to 15min. it shows that the extraction is function of the agitation time. so that a reaction is efficient a necessary time is necessary for the realization of the balance of the extraction.

D. EFFECT OF THE REPORT VOLUMIQUE OF THE ORGANIC PHASE ON THE AQUEOUS PHASE

In this part we compared the extraction of the NaSCN when the aqueous phase and the organic phase are to equal volume and when the volume of the organic phase is superior to the one of the aqueous phase. Salt to extract is to a concentration of 0,001M, the pH of the aqueous phase has been varied by addition of the NaOH. The agent extractant (Aliquat) is to 0,001M. the used diluent is the mixture toluène/acétone. We have to the face 5 the evolution of the extraction rate according to the pH.



Face N°5 : variation of the volume of the organic phase according to the pH

It is clear that the rate of extraction gotten with an organic phase to 25ml is superior to the one gotten to 20ml. Ce result can be justified by the coefficient of distribution, indeed, the rate of extraction being bound to the agent extractant, when the volume of the organic phase is in excess the extractant is sufficiently available in the interface of the food-membrane for the formation of the complex ion extractant. Some similar results have been gotten by [12,13].

E. PHENOMENON OF THE 3RD PHASE ON THE DECANTING

The major inconvenience of certain diluent is the formation of a third phase after extraction what returns the very difficult decanting. The mixture toluène/acétone although efficient present this inconvenience, we notice it in the VI picture or one compared the concentration of salt extracts in the aliquat/toluene and the aliquat/CCL4.

VI picture: Concentration of salts extracted in the organic phase in the aliquat/toluène and the aliquat/CCl4.

Organic phase	[NaSCN] _{org}	[KSCN] _{org}
Aliquat/toluène	0,94.10 ⁻⁴ M	0,83.10 ⁻⁴ M
Aliquat/CCl ₄	0,86.10 ⁻⁴ M	0,49.10 ⁻⁴ M



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According to the results have seen that for an organic phase not only constituted of Aliquat/CCL4 one gets a good output of extraction but also an easy decanting. It would be preferable to do the extraction in Aliquat/CCL4 middle that in Aliquat/toluène middle.

IV.CONCLUSION

To the term of our survey, the various observations all along the done experiences allowed us to enhance the main findings that are the following: The non-miscibility to water and the best solubility of the solution in the toluène makes that this last either the best extractant, the alkali pH encourages the extraction with the ethers-crowns. The aliquat 336 is revealed as the most efficient extractant with a rate of extraction of 94,33%, with one time of agitation of 15minutes. In perspective he/it would be important to achieve this survey on the salts of cyanide in order to make an application to the treatment of the sewages cyanurés rejected by the industrial.

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