CHAPTER 5

Results and Discussion: Extraction of Copper and Nickel

CHAPTER 5

RESULTS AND DISCUSSION: EXTRACTION OF COPPER AND NICKEL

5.1 INTRODUCTION

Extraction of copper from acidic streams is one application of ELMs that has immense potential to be commercialized. Solvent extraction of copper has been practiced for long. At one time it was felt that by end of 1980s half of worlds copper production would use a solvent extraction route. This was not to be due to the slump in metal prices in 1980's and rising costs. Even then a considerable tonnage of copper is produced by liquid extraction route. There are about fifty commercial operations that recover copper from dilute sulfuric acid leach solutions and many more under planning and construction.

Copper solvent extraction plants are an order of magnitude larger than any other type of solvent extraction plant in operation. Usually the annual tonnage of metal produced in a single operation ranges from 5000-80,000 ton/year, flow rate of pregnant liquor 200 – 3000 m^3/hr, surface area of solvent extraction plant $\leq$ 50,000 m^2 (Fisher and Notebaart, 1983). Large sized plants pose typical problems related to design and operation, provision of facilities for preventing accidental discharge to streams and rivers and high capital cost of organic inventory in the plant. All such problems could be addressed by using ELMs.

One of the main advantages of the ELM technique over conventional solvent extraction of metals is that significantly less organic is lost in the raffinate. This feature is of importance particularly in the processing of dilute solutions The U.S. Bureau of Mines has initiated research efforts to use ELMs for extraction of copper from pregnant leach liquor solutions containing 1.43 g/dm^3 of copper and also for mine waters containing about 500mg/dm^3 copper (Wright et al. 1995).

In view of the above possibilities this work was taken up. Copper solution concentration range that was chosen for this work was ≈ 500 mg/dm^3 keeping in view that the utilization of ELM technique would initially be most suitable for treating mine water/ process water that is likely to contain copper in this concentration range. Three copper extractants of rather recent origin namely LIX 84, LIX 84 I and LIX 984 NC were used as carriers in the membrane phase. All of these reagents are chelating type extractants. Moreover, there are no data on copper extraction using ELMs with LIX 84 I and LIX 984 NC as carrier.

Copper is usually extracted from acidic sulfate solutions. However, in solvent extraction literature there are instances of copper recovery from ammoniacal solutions also using chelating reagents. Hence copper was also extracted from ammoniacal solutions using ELMs. Nickel extraction using ELMs have been tried out in literature using Di-2-ethylhexyl-phosphoric acid (D2EHPA). In solvent extraction literature nickel was also extracted from ammoniacal media using chelating reagents. Hence, attempt was made to extract nickel with ELMs, under ammoniacal conditions.

The ELMs were prepared with kerosene as the membrane phase and Span 80 was used as the surfactant like in the previous case for extraction of phenols. Usually sulfuric acid was used as the stripping reagent. The extractants mentioned above were introduced in the membrane (kerosene) phase of the emulsion. The W/O emulsions were characterized by their internal droplet size distribution, viscosity and the interfacial tension registered between the emulsion phase and the external continuous phase.

Experiments were carried out to study the effects of various membrane phase components and process parameters on the extraction of copper. All the extraction results are presented as plots of 'C_e /C_{eo} versus t'. All data Tables for the various extraction runs are reported in Appendix F.

5.2 CHEMISTRY OF METAL EXTRACTIONS

Metal cations can react with organic acids and acidic chelating reagents to form neutral complexes that are preferentially dissolved in the organic phase:

$$M^{2+} + \underline{2RH} \rightleftharpoons \underline{MR_2} + 2H^{+} \qquad (5.1)$$

Where M^{2+} is a bivalent metal cation like copper or nickel, RH is the extractant and the underlined species exist in organic phase.

Reaction step 5.1 describes a cation exchange reaction wherein hydrogen ions are exchanged for the metal cation, so the degree of extraction of metal ions depends on the pH of the external aqueous phase. The degree of extraction will also vary with the nature of the metal. In absence of steric effects, an increasing charge to radius ratio of the metal cation will generally parallel increased extraction.

Metal extraction by acidic reagents is conventionally shown as a stepwise process whereby the reagent partitions between the organic and aqueous phases, ionizes then the acid anion reacts stepwise with the metal ion until the neutral complex is formed that then itself partitions between the two phases:

$$\underline{RH} \rightleftharpoons RH \qquad (5.2)$$

$$RH \rightleftharpoons R^{-} + H^{+} \qquad (5.3)$$

$$M^{2+} + R^{-} \rightleftharpoons MR^{+} \qquad (5.4)$$

$$MR^{+} + R^{-} \rightleftharpoons MR_2 \qquad (5.5)$$

$$MR_2 \rightleftharpoons \underline{MR_2} \qquad (5.6)$$

This conventional description clearly presupposes an extraction mechanism that is wholly dependent on chemical reactions in the aqueous phase requiring at least reasonable water solubility of the extractant. This concept represents one extreme of a spectrum of conditions, the other extreme being wholly interfacial reactions when the extractants are highly water insoluble. In this case steps 5.2 and 5.6 should be replaced by adsorption isotherms relating interfacial concentration of the extractant and metal complex to the bulk phase concentrations. It is fairly well established that for copper extraction using hydroxyoximes (LIX reagents) the kinetically important reactions occur at the interface (Cox and Flett, 1983).

There is considerable disagreement regarding the reaction orders assigned to the reactants (Flett et al.1973, Whewell et al. 1975, Carter and Freiser 1980). This disagreement primarily stems from different experimental techniques used to gather data. The actual rate controlling reaction is still in doubt. Hummelstedt (1980) reported that water exchange on copper ions was rate controlling, supported by the observation that the extraction of copper was faster from chloride than from sulfate solutions. There is general agreement on first-order rate dependence on copper extraction, but no agreement on the pH and reaction order of the extractant concentration.

Extraction of copper by oxime reagents under ammoniacal conditions at high pH values is being increasingly explored since it offers the possibility of a hydrometallurgical treatment of copper sulfide ores and of copper scrap. The chemistry of ammoniacal leaching is complicated. Buffering the solution with ammonium carbonate to maintain pH values of 9 to 10 is common practice. Reagent equilibria at these high pH values favor metal extraction strongly and almost entire capacity of the oxime can be utilized in the formation of 1:2 copper oxime complex as shown below:

$$Cu\,(NH_3)^{2+}{}_4 + 2OH^- + 2H_2O + \underline{2RH} \rightleftharpoons \underline{CuR_2} + 4\,NH_4OH \qquad (5.7)$$

Two features of these high pH extraction systems are undesirable. Firstly oxime loses its selectivity as aqueous phase pH is increased secondly, there is a tendency for free ammonia to transfer to the organic phase which reacts with the sulfuric acid during stripping resulting in ammonium sulfate formation (Whewell and Hanson (1981). Particularly with reference to ELMs where extraction and stripping both occur simultaneously, there is no possibility of washing the organic phase to remove excess ammonia prior to stripping, hence very close control of the pH of the system requires to be maintained.

Nickel extraction from ammoniacal media using oximes has been reviewed by Sole and Cole (2002). Nickel exists in solution as the tetra-, penta-, or hexamine complex, depending on the concentration of free ammonia. The extraction reactions for nickel can be written as follows:

$$Ni(NH_3)^{2+}{}_4 + \underline{2RH} \rightleftharpoons \underline{NiR_2} + 2NH_3 + 2NH_4^+ \tag{5.8}$$

or

$$Ni(NH_3)^{2+}{}_6 + \underline{2RH} \rightleftharpoons \underline{NiR_2} + 4NH_3 + 2NH_4^+ \tag{5.9}$$

The kinetics of nickel stripping from oximes is slow relative to the rate of extraction. As is evident from these reactions, the equilibrium position and extraction of nickel depends on the concentration of free ammonia. Stripping can therefore be achieved by using a solution of strong ammonia and ammonium sulfate or ammonium carbonate to reverse the equilibrium. Alternatively, sulfuric acid may be used for stripping.

5.3 CHARACTERIZATION OF EXTRACTING EMULSIONS.

5.3.1 Internal drop size distribution of W/O emulsion

Internal droplet sizes of emulsions, prepared using kerosene as the oil phase, Span 80 as the emulsifier, LIX 984 NC reagents as the carrier in the membrane phase and H_2SO_4 as the stripping reagent in the internal phase, were measured microscopically at 1500 X magnifications. The concentration of Span 80 and LIX 984 NC in the membrane was 3 % (wt) and 10 % (vol) respectively, both based on the kerosene phase. The concentration of H_2SO_4 in the internal stripping phase (C_{io}) was 1.5 M. The internal phase volume fraction (ϕ) was 0.5. The result is presented as histogram in Fig. 5.1 from which it is observed that 55% of drop sizes were of 1.568 μm , 35 % of 3.136 μm and 10 % of 4.704 μm. The Sauter mean diameter of this distribution d_{32} is 3.424 μm. Fig. 5.2 shows the photomicrographs of the internal droplets from which one can see the clustering of the droplets that make measurements difficult.

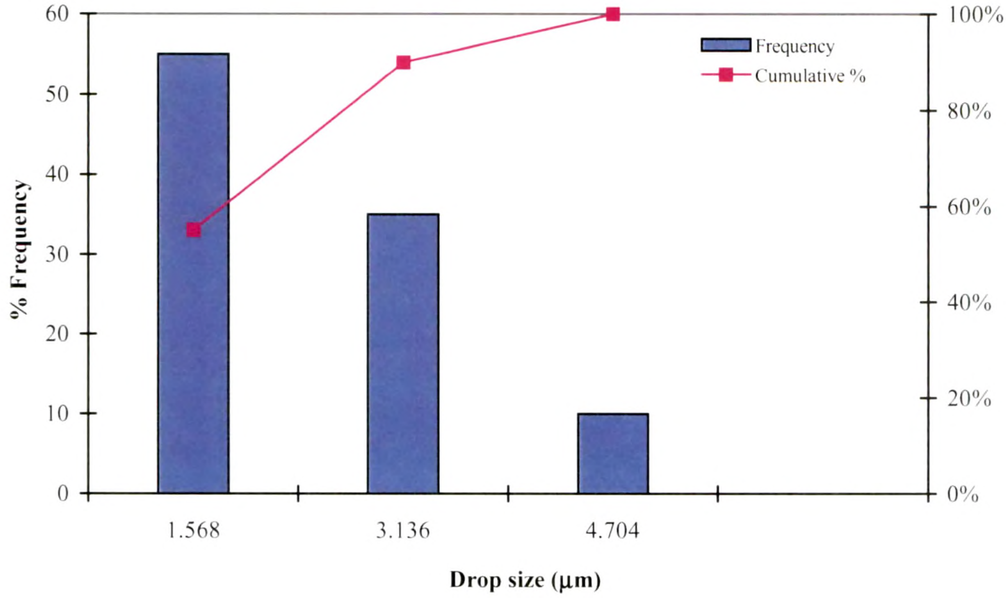

Fig. 5.1: Internal drop size distribution

($\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5$ M, LIX 984 NC = 10%, pH=2)

5.3.2 *Rheological properties of emulsions*

Viscosities of the extracting W/O emulsions were determined using Cone and Plate rheometer as described in Chapter 3. The emulsions were more viscous with H_2SO_4 in the internal phase in comparison with the emulsions prepared for extraction of phenols that contained NaOH solution in the inner phase. Effect of carrier concentration on emulsion viscosities was studied for LIX 84 and LIX 984 NC holding all other parameters of the emulsion constant i.e. surfactant composition $W_{surf} = 3\%$, $C_{io} = 1.5$ M H_2SO_4 and $\phi = 0.5$ Results obtained are presented in Fig. 5.3 and Fig. 5.4 respectively.

It is interesting to find in Fig. 5.3 that the emulsion viscosity increases with LIX 84 concentration up to 7.5 % (vol) then declines at 10 % (vol) and thereafter shows a steady increase. This behavior is observed at all the shear rates investigated in this work. Such behavior was not observed for emulsions containing LIX 984 NC iIt can be seen from Fig. 5.4 that the viscosity progressively increases with reagent concentration. However, it must be noted that the range of concentrations studied was also limited in this case.

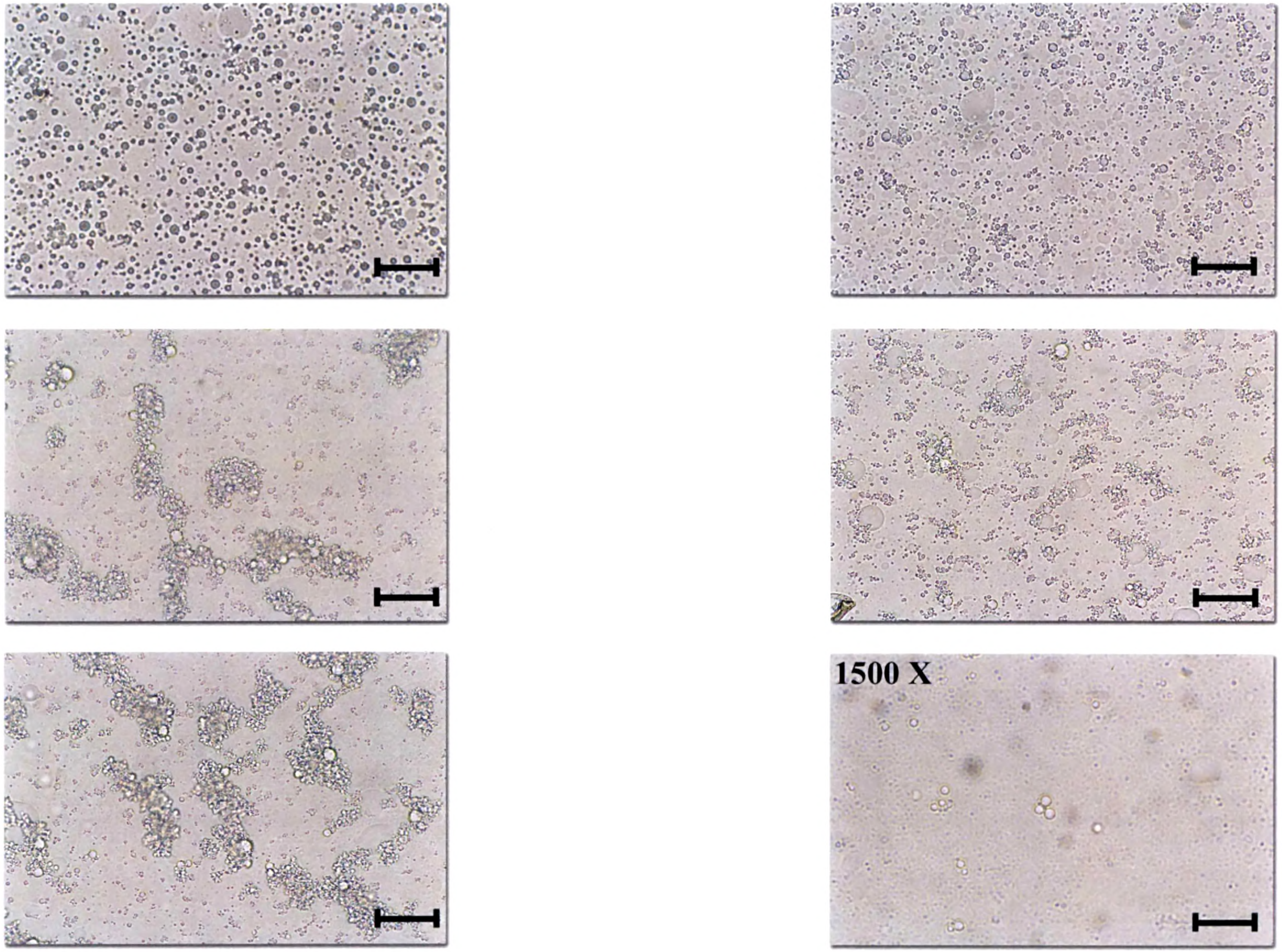

Fig. 5.2: Photomicrographs showing morphological structure of W/O emulsion containing 10% LIX 984 NC as carrier. (∅= 0.5, Span 80=3%, Bar= 10 μm)

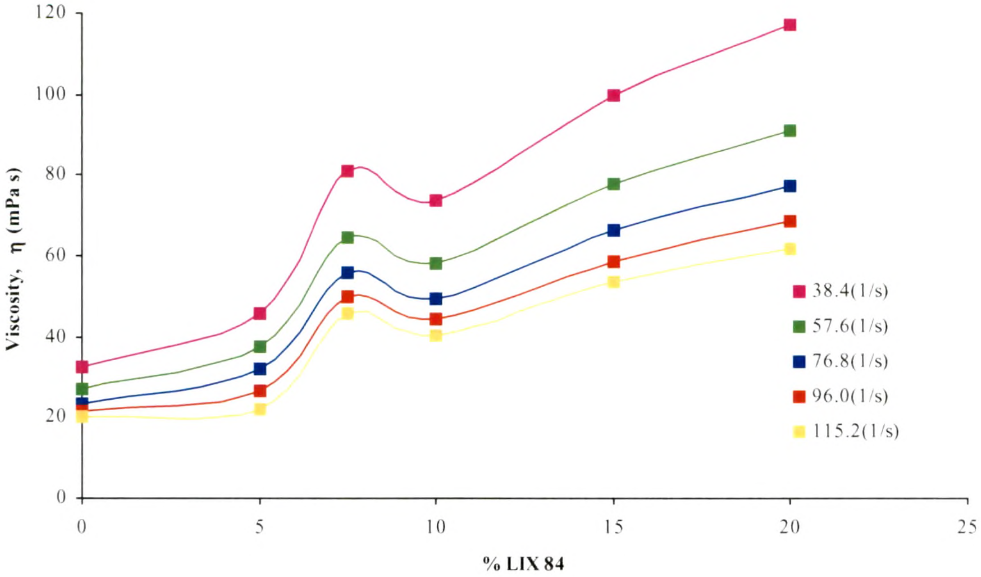

Fig. 5.3: Effect of percentage LIX 84 on viscosity at different shear rates (ϕ=0.5, Span 80 = 3%, C_{io} = 1.5 M)

Viscosities of the W/O emulsions could be conveniently represented by Power law model and also the Bingham model. Table 5.1 lists the values of relevant model parameters and the quality of fit obtained using these two models

Table 5.1: Power law and Bingham parameters for emulsions containing carriers

		Power law model			Bingham model		
Reagent	Vol %	Consistency Index,(mPa.s)	Power law Index	% Fit	Plastic Viscosity (mPa.s)	Yield Stress (mN/m^2)	% Fit
No reagent	---	159.1	0.56	98.9	14.0	7.26	99.5
LIX 84	5	489.4	0.36	95.6	10.3	15.1	94.1
	7.5	533.9	0.40	99.3	28.2	20.7	99.3
	10	542	0.45	99.3	23.7	19.6	99.2
	15	794.8	0.43	99.3	30.0	27.3	99.2
	20	916	0.43	99.7	34.9	31.9	98.8
LIX 984 NC	7.5	624.5	0.45	99.6	27.0	22.7	98.9
	10	653.8	0.45	99.3	28.4	23.7	99.2
LIX 84 I	10	658	0.44	99.5	26.7	23.3	99.1

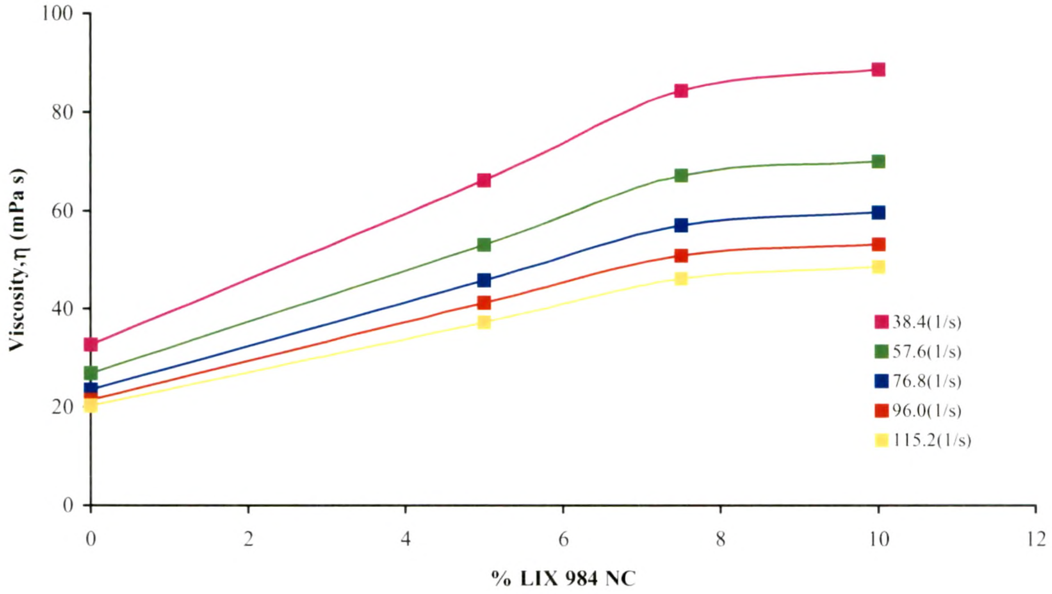

Fig. 5.4: Effect of percentage LIX 984 NC on viscosity at different shear rates (ϕ=0.5, Span 80 = 3%, C_{io} = 1.5 M)

5.4 DISPERSION BEHAVIOR OF EMULSIONS

The extracting W/O emulsions containing LIX reagents as carriers were dispersed in the copper containing media at different stirring speeds. It was observed that at stirring speeds of 160 rpm the emulsion got finely dispersed in the aqueous media with the formation of tiny globules that were very distinct. The globule sizes on the whole were much smaller than the globules observed for the case of the W/O emulsions used for extraction of phenols.

Interfacial tension values are listed herewith for emulsions containing LIX 84 as the carrier with the membrane parameters being $\phi = 0.5$, $W_{surf} = 3\%$, $C_{io} = 1.5$ M H_2SO_4 and the pH of the external phase being 2.

LIX 84 concentration (Vol %)	0	5	10	20
Interfacial Tension (mN/m)	6	7	8	10.5

Comparing these values with those listed in Table 4.6 one could make out that the difference in globule sizes stems from the difference in the interfacial tensions between the emulsion and the continuous phase

It is known that oximes have a tendency to accumulate at the aqueous-organic interface but not to the extent expected of a true surface-active agent. The lowering of interfacial tension by addition of an extractant is the result of the penetration of the interfacial surface by hydrophilic groups. The mutual repulsion of these polar groups causes the contractile tendency of the interface to be reduced. The interfacial tension depends on the regent type, bulk phase concentration, diluent and the water solubility of the reagent. (Cox and Flett 1983)

Interfacial tension showed an increasing trend with an increase in the carrier concentration in the ELMs that is contrary to the expected behavior between oil containing surfactant and an aqueous solution. This could be possibly due to an increased proportion of oxime in an aggregated form. The aggregates are known to be less surface active than the oxime monomer. In view of absence of data on interfacial tensions between extracting emulsions containing oximes and aqueous phase and also the complex nature of emulsions, it is difficult to comment on this aspect. Interfacial tensions are reported to be constant between 2 to 6 pH.

Emulsions containing 10 % LIX reagents in the oil phase, having $\phi = 0.5$, $W_{surf} = 3\%$, $C_{io} = 1.5$ M H_2SO_4 were dispersed in aqueous media containing $\approx$ 500mg/dm^3 of copper at 160 rpm. The treat ratio was maintained at 1:6. The dispersions were photographed at definite interval of time and globule sizes were measured using imaging software Photoshop 7. Fig. 5.5 shows the dispersion history for emulsions containing LIX 84. The droplet sizes were almost uniform in size in the first half hour of contact thereafter they registered increase in size due to swelling.

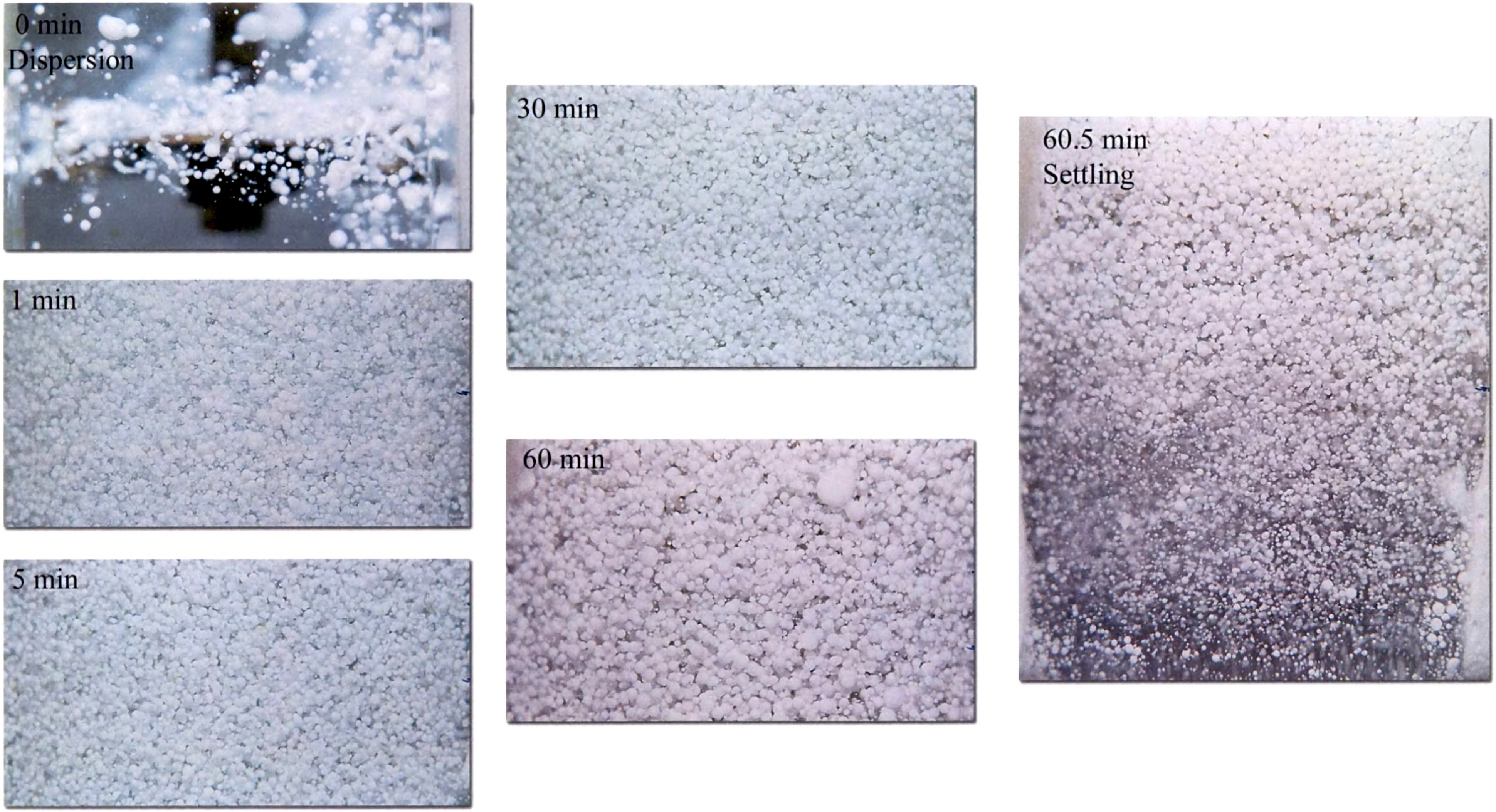

Fig. 5.5: Snapshots showing dispersion history of emulsion globules containing LIX 84 carrier for copper extraction from sulfate media (N=160 rpm, Ø 0.5, pH=2)

Fig. 5.6 shows the globule size distribution at 10 minutes interval for this particular case. It is observed that the dominant globule size is 0.227 mm that has a frequency of 47 %. While the largest globule size is 1.136 mm that has only 1 % frequency.

The Sauter mean diameter d_{32} for this distribution turns out to be 0.540 mm. It is interesting to note that substituting the experimentally obtained values of interfacial tension reported above in the Ohtake *et al.* correlation, the predicted values of d_{32} turn out to be 0.559 mm a reasonably close fit.

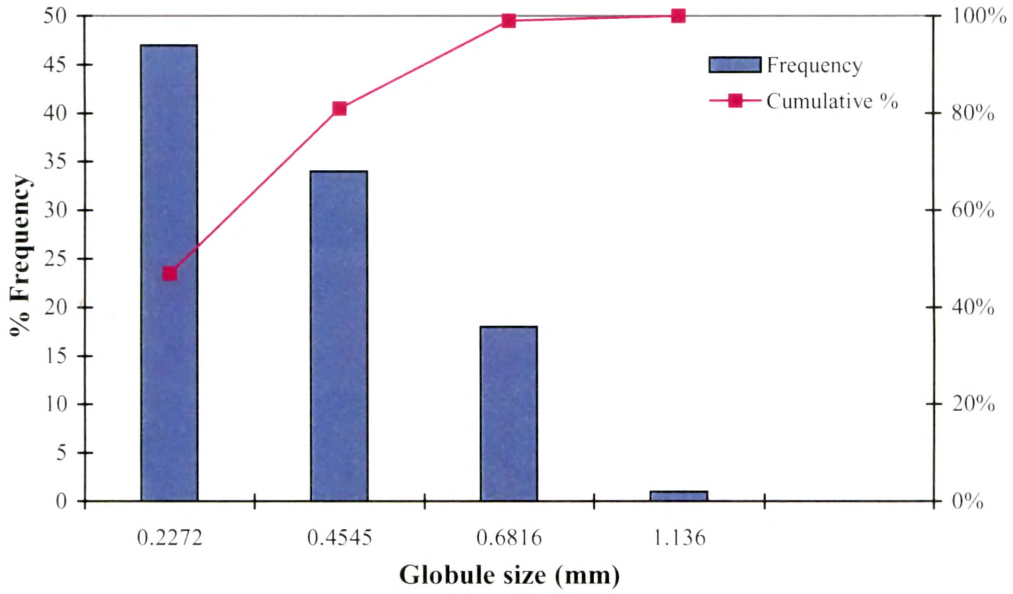

Fig. 5.6: Globule size distribution for extraction of copper with LIX 84 in sulfate media

(N= 160rpm, ϕ = 0.5, Span 80 = 3%, C_{io} = 1.5M, TR = 1:6, C_C = 10%, pH = 2)

Similarly the dispersion behavior of emulsions containing 10 % LIX 984 NC were studied keeping all other emulsion and process parameters identical. Fig. 5.7 shows the dispersion history of the emulsion globules for this case. One noteworthy observation was the globules in this case were perfectly spherical and very distinct. The obscurance in the case of emulsions containing LIX 984 NC was the least amongst all the emulsions studied in this work.

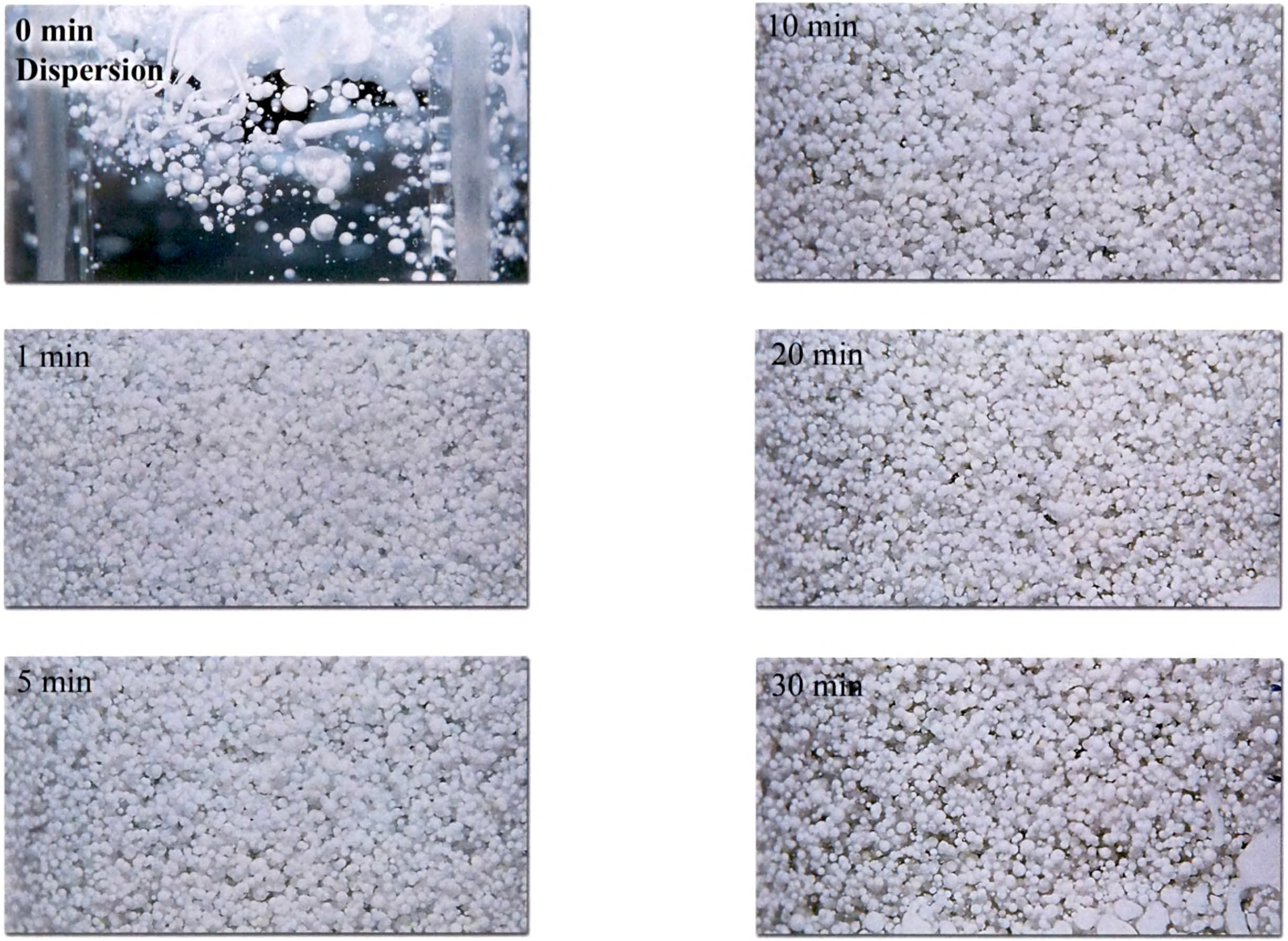

Fig. 5.7: Snapshots showing dispersion history of emulsion globules containing LIX 984 NC carrier for copper extraction from sulfate media at N=160 rpm. (ϕ 0.5, pH=2)

Fig. 5.8 shows the globule size distribution for emulsions containing LIX 984NC. The dominant globule size was 0.454 mm, the d_{32} for this distribution was calculated to be 0.678 mm. Emulsions containing LIX 84 I was dispersed in ammoniacal media. The ammoniacal copper complex was intense blue in color at pH = 8.1. All other emulsion and process parameters remained the same.

Fig 5.9 shows the dispersion history for LIX 84 I in ammoniacal media the time span of observation was just 3 minutes due to complete removal of copper in that time frame. The globule size distribution was evaluated at 1 min sampling time and is reported in Fig. 5.10. The Sauter mean diameter for this distribution turns out to be 0.436 mm.

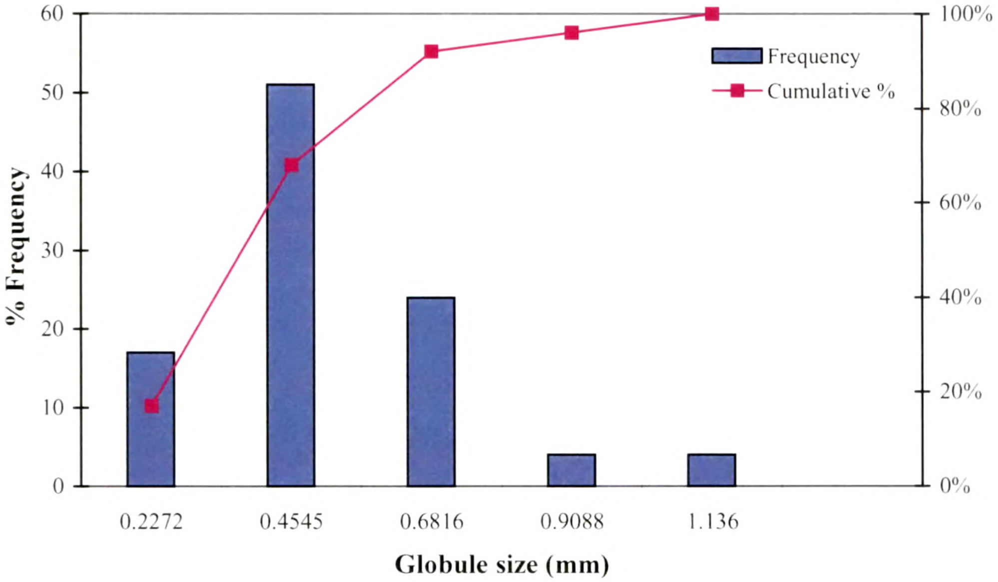

Fig. 5.8: Globule size distribution for extraction of copper with LIX 984 NC in sulfate media

(N= 160rpm, ϕ = 0.5, Span 80 = 3%, C_{io} = 1.5M, TR = 1:6, C_C = 10%, pH = 2)

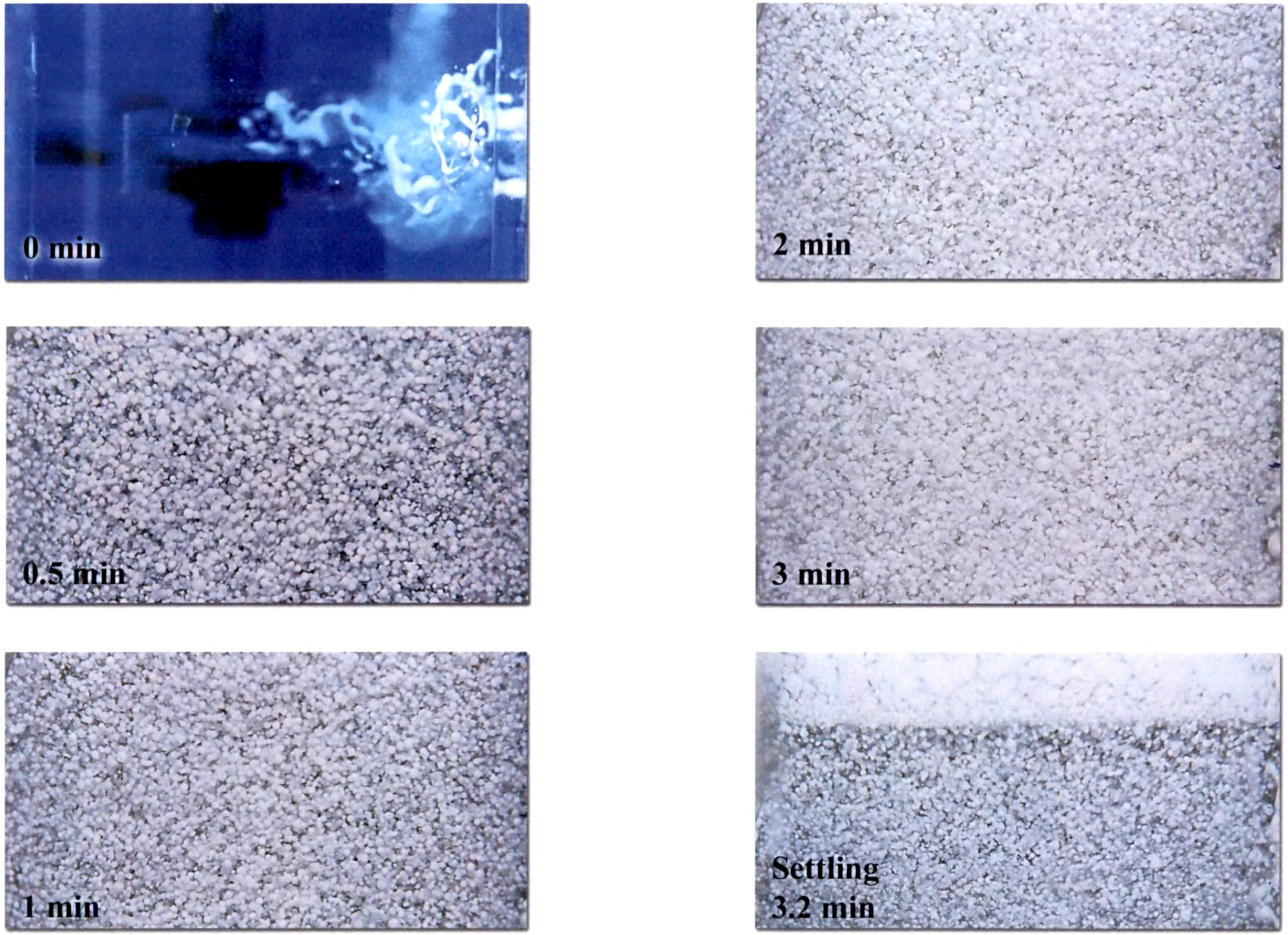

Fig. 5.9: Snapshots showing dispersion history of emulsion globules containing LIX 84-I for copper extraction from ammoniacal media ($N = 160$ rpm $\varnothing = 0.5$, $pH = 8.1$)

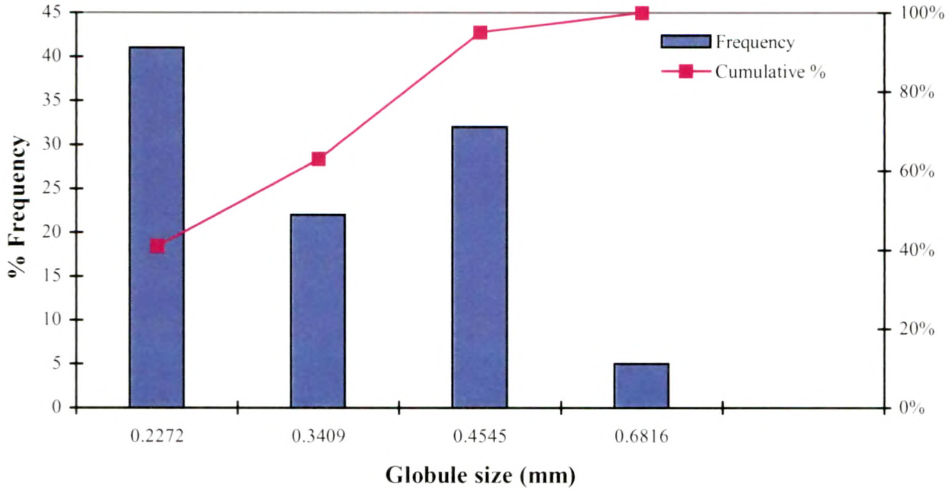

Fig. 5.10: Globule size distribution for extraction of copper with LIX 84I (N= 160rpm, $\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5M$, TR = 1:6, $C_C = 10\%$)

5.5 EXTRACTION OF COPPER USING ELMs.

The chelating extractants LIX 84, LIX 84 I and LIX 984 NC were used as carriers in the membrane phase of the ELMs to extract copper from sulfate media. Further both copper and nickel were also extracted from ammoniacal media using LIX 84 I as carrier. In all the extraction runs carried out the W/O emulsion had an internal volume fraction $\phi = 0.5$ except when the effect of ϕ was studied. Similarly the Treat ratio was usually maintained as 1:6 except where its variation was studied. The carrier concentration was usually 10 % vol. of the membrane phase except when variation in carrier concentration was studied. The concentration of copper in external phase was about 500 mg/dm^3.

5.5.1 Effect of stirring speed

In order to select the stirring speeds for experimental runs, initial experiments were carried out at different stirring speeds. The extracting W/O emulsion prepared using LIX 84 as the carrier with the above mentioned membrane composition were much more viscous in comparison to the emulsions used for extraction of phenols and hence dispersion at 135 rpm was very poor. Increasing the stirring speed to 155 rpm dispersed the emulsion finely.

Pilot runs suggested that it would be necessary to continue extraction for greater duration of time for metal extraction in comparison with extraction of phenols. Increased time of contact between the emulsion and aqueous phase necessarily results in greater swelling. Swelling increases the viscosity of the emulsion that results in poor dispersion at the later phase of the run. Hence it was thought appropriate to agitate the dispersion at stirring speeds slightly more than 155 rpm. Maintaining stirring speed of 160 rpm not only dispersed the emulsion finely but also maintained the nature of the dispersion uniform throughout the duration of the run. Experiments were also carried out at stirring speeds of 190 rpm.

Fig. 5.11 compares the extraction at 160 rpm with that at 190 rpm, for both these runs the internal phase reagent concentration was 1 M and the external phase containing copper was maintained at pH = 2. It can be seen that at all sampling times the experiment at 190 rpm extracted more copper. As time duration of the run increased the gap between the two curves continually decreased, almost converging at sixty minutes. In spite of the better extraction performance of the 190 rpm run it was felt appropriate to perform all subsequent experiments at 160 rpm in view of the excessive swelling that occurred at 190 rpm.

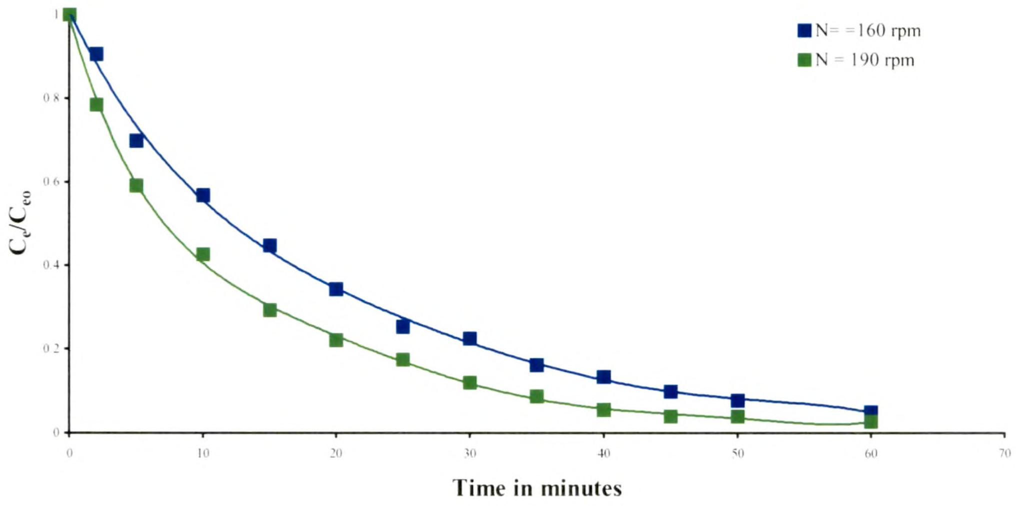

Fig. 5.11: Effect of stirring speed on extraction of copper from sulfate media using LIX 84

(ϕ = 0.5, Span 80 = 3%, C_{io} = 1.0M, TR = 1:6, C_C = 10%, pH = 2)

5.5.2 Effect of C_{io}

The internal phase acid concentration in the emulsion is a very important parameter since it decides the capacity of the emulsion to extract the solute. In Type I transport mechanism there is a direct relationship between internal phase reagent concentration and the amount of solute extracted. In carrier mediated Type II transport mechanism such direct relationship cannot be established and this is in view of the fact that it is the presence of the carrier that brings about the extraction. The nature of the carrier and its concentration influence the extraction to a greater degree in comparison with the influence of $C_{io.}$

However, once the carrier type and concentration is selected then the internal phase concentration C_{io} could be conveniently tuned to increase the capacity of the ELMs and the rates of extraction within the limits of membrane stability. Emulsions were formulated using kerosene as the membrane phase, LIX 84 as the carrier, sulfuric acid as the inner stripping phase and Span 80 as the surfactant. The emulsions had $\phi = 0.5$, $W_{surf} = 3$ % (wt) of the oil phase and carrier concentration $C_C = 10$ % vol. of the oil phase. The emulsion was dispersed in the continuous phase at 160 rpm, maintaining Treat ratio 1:6.

Three variations in the internal phase concentration were tried out, Fig. 5.12 shows the extraction curves at C_{io} of 1 M, 1.5 M and 2 M. There is a substantial increase in the rates of extraction with an increase in C_{io} from 1M to 1.5 M. Further increase in C_{io} to 2 M increases the rate of extraction but not to the extent that is observed in the first case. The curve for 2 M plateau at 30 minutes while that of 1.5 M plateau out at 45 minutes when both these curves merge. Merger is expected because external phase concentrations are identical in all three cases and the internal phase reagent capacity is in excess of the stoichiometric requirement. The extraction at $C_{io} = 1$ M is the slowest but this curve too tends to converge with the other two curves at 60 minutes duration.

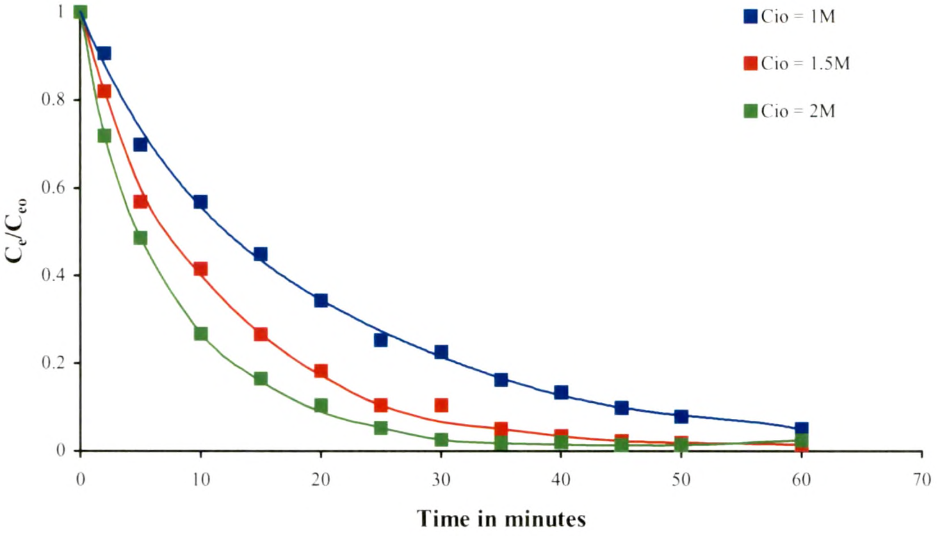

Fig. 5.12: Effect of C_{io} on extraction of copper from sulfate media using LIX 84 (N= 160rpm, $\phi = 0.5$, Span 80 = 3%, TR = 1:6, $C_C = 10\%$, pH = 2)

The difference in the curves in Fig. 5.12 essentially stem from the different rates of stripping obtained with differing acid concentrations in the internal phase of the W/O emulsion since all other parameters are the same in the three runs. It was surprising that Völkel *et al.* (1980) in their investigation on copper removal using LIX 64N did not observe an effect of the stripping phase concentration in the initial duration of the run. Solvent extraction literature (Whewell and Hanson 1981) indicates a direct first order dependence of the rate on the aqueous acid concentration and on the organic-phase copper concentration. The nature of diluents shows a definite trend on the rates of stripping: paraffins > napthenes >aromatics but within each class, the solution viscosity is an important factor in determining the rate.

One unique feature observed with the emulsions containing different C_{io} was that the viscosity of the emulsion passed through a maxima. Thus at shear rate of 38.4 s^{-1} the viscosities obtained were 65.4 mPa.s, 73.9 mPa.s and 59.03 mPa.s for C_{io} values of 1 M, 1.5 M and 2 M respectively. The relatively lower viscosity for the case of emulsions with C_{io} = 2 M is perhaps an additional reason for greater removal of copper in this case since copper complex would have lower diffusivity in the more viscous emulsion.

Although C_{io} = 2M showed faster extraction in comparison with C_{io} = 1.5M but the corrosion that was observed in the rheometer cup with emulsions containing 2M acid in inner phase prompted working with lower acid concentration in the membrane phase or else the emulsion viscosity would not have been possible to measure. Taking into account the remarkable increase in the extraction rates on increase of the C_{io} from 1 M to 1.5 M it was decided to maintain the internal stripping phase H_2SO_4 concentration at 1.5 M in the subsequent investigations.

5.5.3 Effect of surfactant concentration

Effect of surfactant concentration was investigated with 3 % (wt) and 4.7 %(wt) Span 80 in the membrane phase using ELMs containing 10 % (vol.) LIX 84 and keeping all other parameters unchanged i.e. $\phi = 0.5$, $C_{io} = 1.5$ M, $W_{surf} = 3$ %, TR = 1:6, N =160 rpm, $C_{eo} \approx 500$ mg/dm^3 and the external phase pH = 2 . The results are presented in Fig. 5.13. It is seen that increase in surfactant concentration leads to a decrease in the amount extracted when $W_{surf} = 4.7$ %.

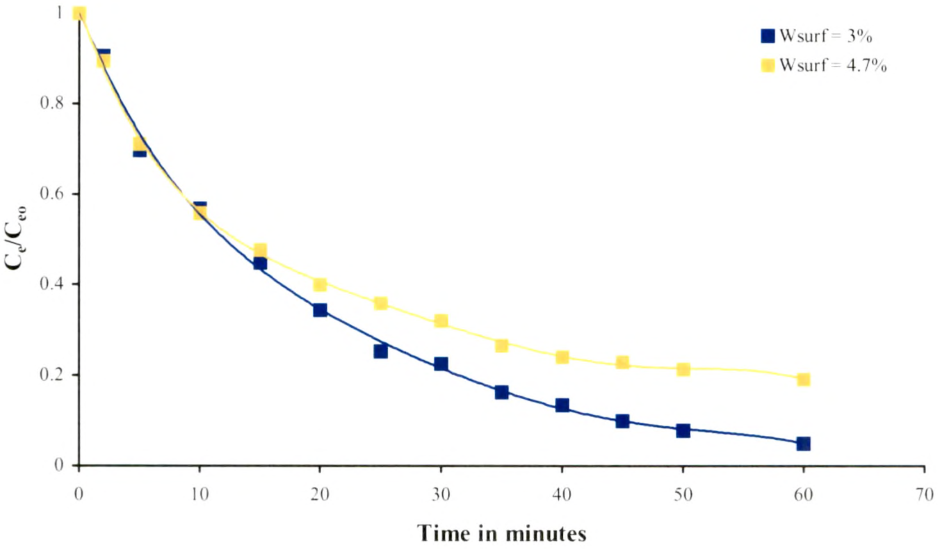

Fig. 5.13: Effect of surfactant concentration on extraction of copper from sulfate media using LIX 84

(N= 160rpm, $\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5$M, TR = 1:6, $C_C = 10\%$, pH = 2)

This decrease in the copper extracted could be attributed to a number of possible factors including 1) decrease in the rate of copper complexation at the membrane phase- external phase interface, caused due to decrease in the interfacial population of the carrier because of high interface occupancy of the surfactant. 2) An increase in the interfacial viscosity. 3) A decrease in the movement of internal – phase droplets within the emulsion globules. Mikucki and Osseo-Asare (1986) also observed similar behavior for copper extraction using ELMs containing LIX 65N-LIX 63 mixtures with variation in Span 80 and a number of other emulsifiers.

5.5.4 Effect of internal phase volume fraction ϕ

Effect of ϕ was investigated using ELMs containing LIX 84 as the carrier, other emulsion and process parameters were maintained constant with $C_C = 10$ % (vol), Cio = 1.0 M, $W_{surf} = 3$ %, TR = 1:6, N =160 rpm, $C_{eo} \approx 500$ mg/dm^3 and the external phase pH = 2. Three variations of ϕ was studied $\phi = 0.4$, $\phi = 0.5$ and $\phi = 0.6$. The results are presented in Fig. 5.14. It is observed that an increase in ϕ results in an increase in the rates of extraction.

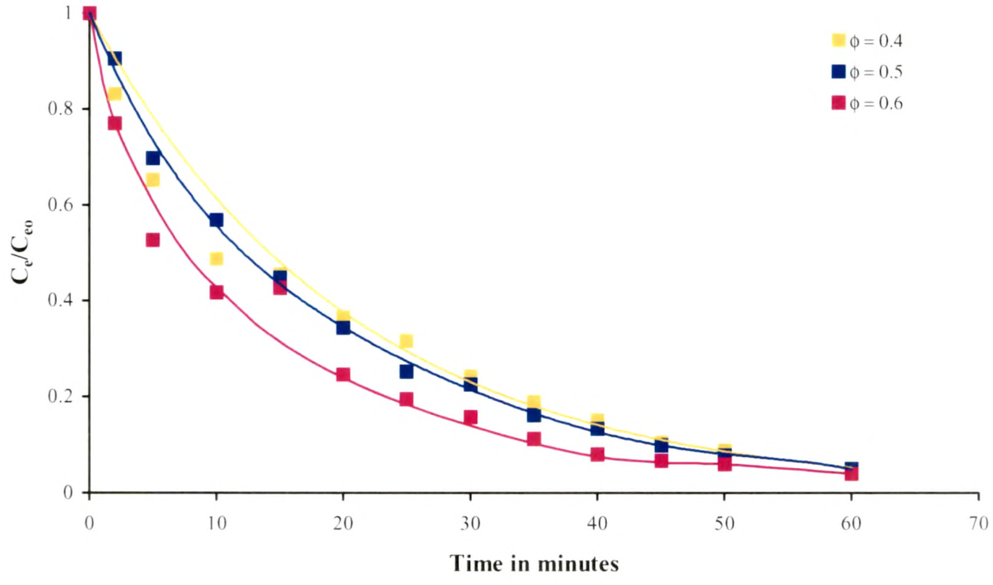

Fig. 5.14: Effect of ϕ on extraction of copper from sulfate media using LIX 84 (N= 160rpm, Span 80 = 3%, $C_{io} = 1.5$M, TR = 1:6, $C_C = 10\%$, pH = 2)

This increase in rates is not significant when ϕ increases from 0.4 to 0.5 but is quite substantial when ϕ further increases to 0.6. The fact that all three curves merge at the same concentration at the end of the run signifies that almost same extent of removal takes place in each case. Further in all three cases the stripping phase capacity was much more than the stoichiometric requirement. Moreover, since the concentration of H_2SO_4 was constant for all three cases it implied that the stripping phase reagent did not play a dominant role. Hence it could be inferred that with increase in ϕ there is a considerable decrease in the path length that the copper- oxime complex has to traverse within the globules prior to getting stripped. This decrease in path length causes the increase in the rates of extraction with increasing ϕ.

It is interesting to note that the extraction rate with ELMs having $\phi = 0.6$, $C_{io} = 1.5$ M and stirring speed of 160 rpm coincides with the extraction rates with $\phi = 0.5$, $C_{io} = 1.0$ M and stirring speed of 190 rpm as shown in Fig. 5.15. This indicates that ELMs can be tailored to achieve a particular performance level using different variables.

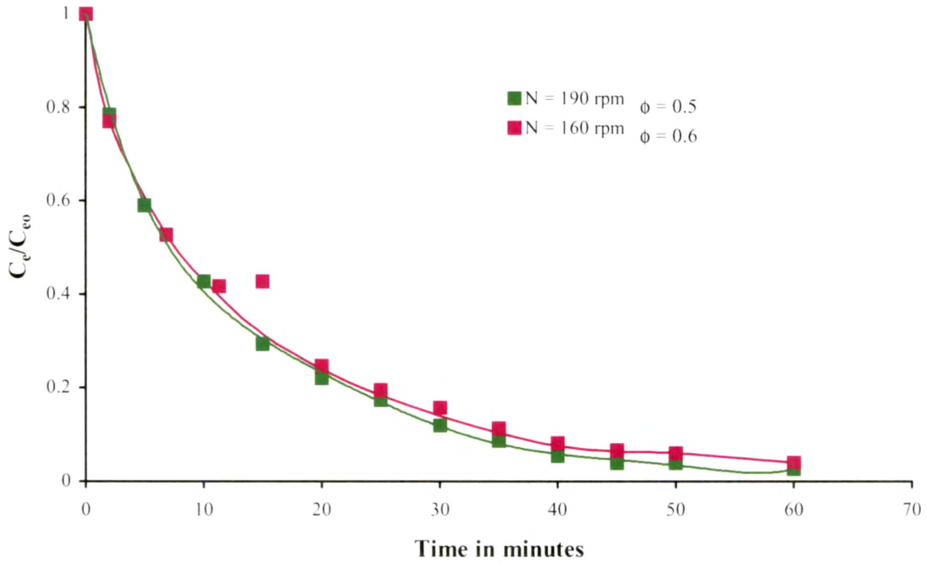

Fig. 5.15: Effect of ϕ and stirring speed on extraction of copper from sulfate media using LIX 84

(Span 80 = 3%, C_{io} = 1M, TR = 1:6, C_C = 10%, pH = 2)

5.5.5 Effect of carrier concentration

Carrier concentration plays a vital role in the overall extraction behavior of ELM systems. The effect of carrier concentration was investigated for the case of two carriers LIX 84 and LIX 984 NC under otherwise identical conditions. All runs were carried out with the conditions $\phi = 0.5$, $C_{io} = 1.5$ M, $W_{surf} = 3$ %, TR = 1:6, N =160 rpm, $C_{eo} \approx 500$ mg/dm^3 and the external phase pH = 2. Five variations of concentration were studied for LIX 84 while three variations of concentrations were investigated for LIX 984 NC. The results of the investigation are presented in Fig. 5.16, where the concentration curves are colour coded and the same color code applies to LIX 84 as well as to LIX 984 NC. The filled lines in the figure represent LIX 84 extraction curves while the dotted lines apply to LIX 984 NC.

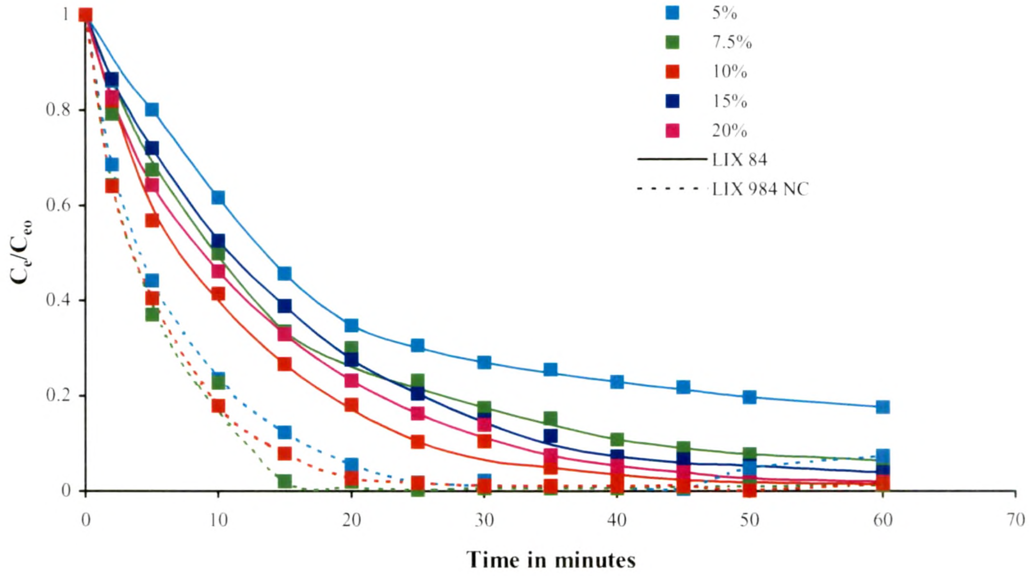

Fig. 5.16: Effect of % LIX concentration on extraction of copper from sulfate media using LIX 84, and LIX 984 NC

(N= 160rpm, $\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5$M, TR = 1:6, pH = 2)

It is seen in Fig 5.16 that an optimal in carrier concentration exists in these extractions. For ELMs using LIX 84 as carrier it was observed that with increase in C_C from 5%(vol) to 7.5 % (vol) to 10% (vol) there was an progressive increase in extraction rates and corresponding increase in copper removal. Further, increase in the C_C to 15 %(vol) and 20 %(vol) resulted in a decline in extraction rate and the amount extracted.

This behavior of extraction rates could be correlated with the rheological behavior of emulsions observed in Fig. 5.3, where a sudden decrease in viscosity was observed at 10 % (vol) of LIX 84 carrier in the membrane phase. Increase in the viscosity at C_C of 15 %(vol) and 20 % (vol) makes the globule diameter large, the diffusivity of the copper complex low and the internal resistance more. This type of behavior was also observed by Teramoto et al.(1983) for copper extraction using ELMs containing SME 529 as carrier.

Another important factor that could be contributing to this behavior is the aggregation nature of the oximes. Organic compounds containing donor atoms capable of complexing metal ions exhibit interactions between their molecules when in solution in organic diluents of low dielectric constant and low hydrogen bonding ability. The presence of intermolecular bonding in oxime solutions was noticed in seventies, vapor phase osmometery measurements confirmed the existence of aggregates in solutions of oximes.

Aggregates larger than dimers are formed in aliphatic hydrocarbons but in presence of diluents of greater hydrogen bonding capability a reduction in mean aggregation number is observed. The mean aggregation numbers of all the oxime systems are very dependent on the total concentration of oxime in the solution; hence several species are expected to be in dynamic equilibrium, probably a monomeric oxime at equilibrium with one or more aggregated species. Increase in the oxime concentration leads to an increased proportion of oximes in an aggregated form the aggregates are less surface active than the monomers hence tend to stay away from the surface.

As the oxime concentration is increased, plot of interfacial tension versus log (oxime concentration) deviates from straight line, Whewell and Hanson (1981) attribute this deviation to the increasing proportion of oxime in an aggregated form. It is interesting to note that interfacial tensions reported in Section 5.4 shows an increase with increasing LIX 84 concentration in the membranes.

Experiments with ELMs containing LIX 984 NC also showed identical behavior, as but not so pronounced as in the case of LIX 84. It can be observed in Fig.5.16 that the extraction is marginally higher with carrier concentration C_C = 7.5 % than that obtained with carrier concentration of 10 %. Another glaring feature that is revealed in the above mentioned figure is the huge enhancement in rates with the use of LIX 984 NC in comparison with LIX 84. This difference fundamentally stems from the large amount of 5-dodecylsalicylaldoxime a very strong copper extractant present in LIX 984 NC.

5.5.6 Effect of Treat ratio

Effect of variation in Treat ratio TR was studied using ELMs containing LIX 84 carrier in the membrane phase all other parameters were maintained constant i.e. C_C = 10 % (vol), Cio = 1.5 M, W_{surf} = 3 %, ϕ = 0.5, N =160 rpm, $C_{eo} \approx 500$ mg/dm^3 and the external phase pH = 2. Treat ratios were varied in the range of 1:10 to 1:4. Increase in the treat ratio leads to an increase in the dispersed phase holdup, hence it results in an increase in the overall extraction capacity. Increase in Treat ratio is also expected to increase the rate of extraction due to increase in the amount of carrier in the system and the overall surface area for mass transfer. The extraction curves for Treat ratio variation are presented in Fig. 5.17.

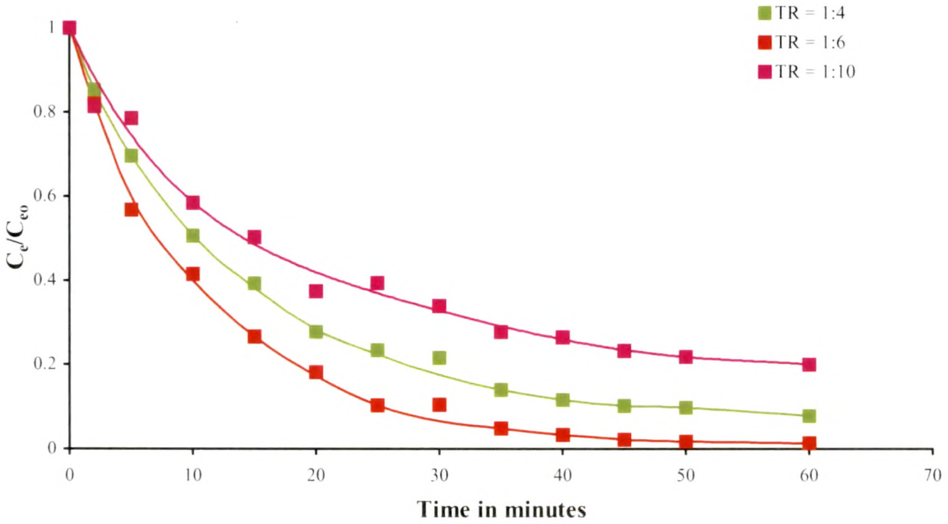

Fig. 5.17: Effect of Treat ratio on extraction of copper from sulfate media using LIX 84 (N= 160rpm, ϕ = 0.5, Span 80 = 3%, C_{io} = 1.5M, C_C = 10%, pH = 2)

At the lowest Treat ratio experimented i.e. at TR = 1:10, the extent and rate of extraction was the least as expected. It was surprising to find that at TR = 1:4 the rates and extent of extraction were less than that obtained for TR = 1:6. It is difficult to explain such wrong way behavior .One possible reason could be that the large volume of dispersed phase caused large increase in globule size resulting in a decrease in the mass transfer rates.

5.5.6 Effect of external phase concentration

The effect of copper concentration in the external phase on extraction behavior was investigated at two concentrations. Performance of the two carriers LIX 84 and LIX 984 NC was investigated. The emulsion and process conditions were identical in these runs. The conditions maintained were, C_C = 10 % (vol), ϕ = 0.5, C_{io} = 2M, W_{surf} = 3 % N =160 rpm, and the external phase pH = 2. The results are presented in Fig.5.18

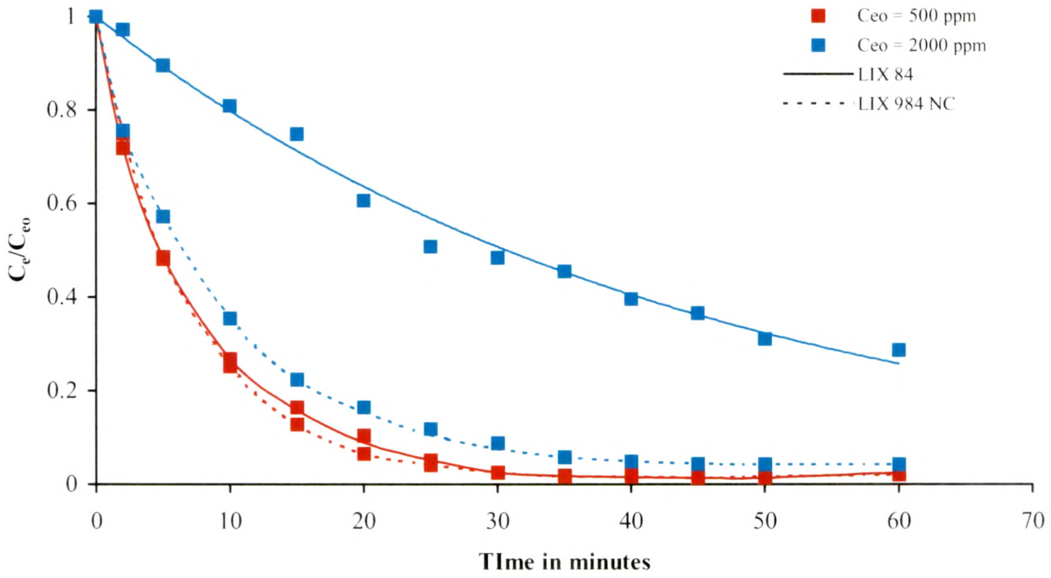

Fig. 5.18: Effect of initial concentration on extraction of copper from sulfate media using LIX 84 and LIX 984 NC

(N= 160rpm, ϕ = 0.5, Span 80 = 3%, C_{io} = 2M,TR = 1:6, C_C = 10%, pH = 2)

It is seen in Fig 5.18 that with membranes containing LIX 84 there is a wide gap between the extraction curves when C_{eo} = 460 mg/dm^3 and 1880 mg/dm^3. Such gap does not exist with membranes containing LIX 984 NC when the values of C_{eo} are 465mg/dm^3 and 1903 mg/dm^3 respectively. The reason for such wide gap in the case of LIX 84 stems from its being a ketoxime which is moderately strong copper extractant and kinetically slow.

In order to overcome the shortcomings of ketoximes the salicylaldoximes were developed. Their outstanding characteristics include rapid copper transfer and high extractive strength. However, the salicylaldoximes by themselves are such strong copper extractants that they are most often used in combination with a ketoxime so that they can be efficiently stripped. As a group salicylaldoximes are less stable than ketoximes and within salicylaldoxime subgroup, the nonyl derivative is less stable than the dodecyl derivative. LIX 984 is a ketoxime – salicylaldoxime mixture which has the extractive strength and fast kinetics of the salicylaldoximes combined with the excellent physical performance and stability of the ketoximes (Redbook 1997,2001).

The reagent LIX 984 NC used in these investigations is a concentrated version of LIX 984 and has an oxime concentration of 2.29M. Hence the performance does not decline even though there is a four-fold increase in solute concentration. There is quantitative removal in both cases. Thus membranes containing LIX 984 NC could be used over a wide range of solute concentrations with almost the same performance levels in each case provided the capacity of the stripping acid is sufficient for the stripping the solute extracted. Such expectations cannot be fulfilled by ketoxime extractants. LIX 984 NC opens up avenues for the use of ELMs for the extraction of copper not only from dilute solutions but also from sulfuric acid leach solutions and at par with the conventional solvent extraction techniques.

5.5.7 Effect of pH of external phase on extraction.

It is well known that the pH of continuous phase has a profound influence on extraction behavior. Although almost all the chelating agent form extractable metal complexes with a large number of metals, the reaction may be rendered selective, or even specific for the targeted metal, by a proper adjustment of the initial aqueous solution. Since the chelating LIX reagents (oximes) are weak acids ($pK_a = 10.7$ for salicylaldoxime and $pK_a = 10.5$ for ketoxime), the formation of the extractable complexes will much depend on the pH of the aqueous solution. Thus the simplest way is to affect the equilibrium by adjustment of the aqueous pH. This procedure is useful for extractive separation of metals whenever the equilibrium constants are sufficiently different for the metal in question.

Since the extractability of the metal is directly proportional to the mth power of the hydrogen ion concentration $D = K\ [\ \underline{RH}\ ]^m\ [H^+]^{-m}$, hence at any given organic-phase composition , the distribution ratio can be evaluated from the known equilibrium constant K. The effect of pH will be obviously different for a different charge on the extractable metal ion, m. The distribution ratio will increase by a factor of 10 for a monovalent cation, by a factor of 100 for a divalent and a factor of 1000 for trivalent cation, when, the pH of the aqueous solution is altered by one unit.

The pH isotherms for chelating extractants and acidic extractants are reported in literature (Cox and Flett 1983, Redbook 1997,2001, Sole and Cole 2002) and could be conveniently used to design extraction systems. The pH value for which extraction is 50 % at a given extractant concentration is called pH_{50}. In the extraction of two metals of equal charge *m* with a given extractant, if $|\ pH_{50}{}^1 - pH_{50}{}^2\ | \geq 3$, the metals are readily separated at equal phase volumes with maximum 1 % contamination. Selecting a pH value1.5 units higher than the pH_{50} for a given metal will ensure a practically quantitative extraction of this and all the more extractable metals present in the solution. Stripping with an aqueous solution of pH 1.5 units less than pH_{50}, ensures that only the wanted metal will return to the aqueous phase, while the much more extractable metals will remain in the organic phase (Marcus and Kertes 1969).

Based on the above-mentioned considerations and the product information literature supplied by Cognis (Redbook 1997,2001) for the LIX reagents, the pH of aqueous phase for extraction of copper was maintained pH = 2. Extraction was also carried out at pH = 5 and at pH = 1.The external phase pH was balanced by the addition of 1 M H_2SO_4 to the continuous phase under constant stirring conditions. In order to obtain pH 5 the solutions were first made acidic and subsequently the pH increased by addition of Na_2CO_3.

The three chelating extractants LIX 84 I, LIX 84 and LIX 984 NC were used individually as carriers in the ELMs. Extraction using LIX 84 I was performed at pH 2 and pH=5 only. Further the acidic extractant CYANEX 302 (Bis (2,4,4- trimethyl- Pentyl)-monothio phosphonic acid) that is known to extract copper quantitatively at pH 1.39-2.10 was also used as a carrier in ELMs that extracted copper at 2 pH. The results of these 10 extraction runs are presented in Fig.5.19. This figure in a way also compares the four extractants studied in this work.

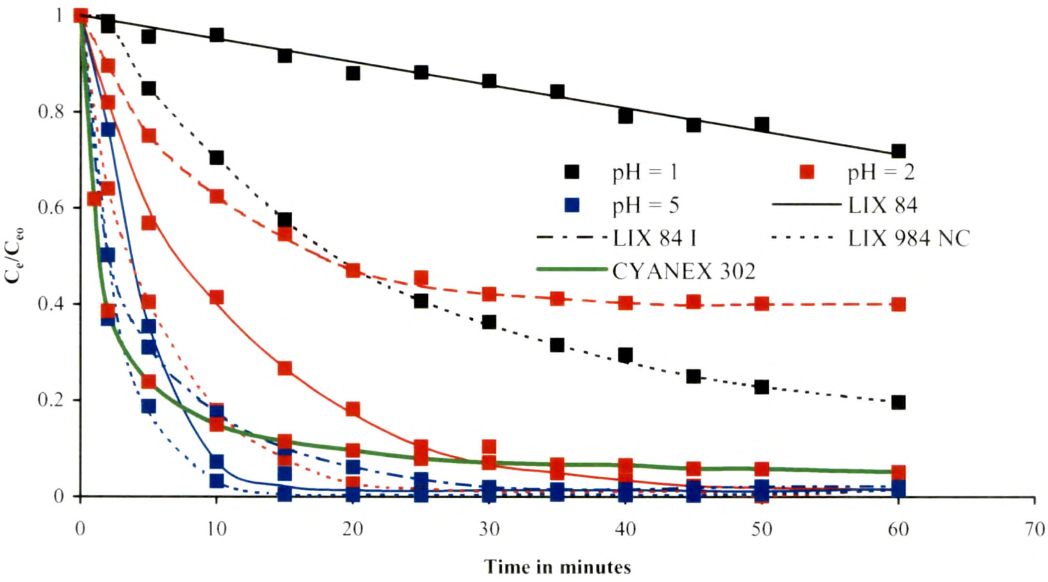

Fig. 5.19 Effect of pH on extraction of copper from sulfate media using different carriers

(N= 160rpm, ϕ = 0.5, Span 80 = 3%, C_{io} = 1.5M, TR = 1:6, C_C = 10%, pH = 2)

In all these experiments the emulsion and process conditions that were maintained are the following : C_C = 10 % (vol), ϕ = 0.5, Cio = 1.5 M, W_{surf} = 3 %, N =160 rpm, and the external phase copper concentration $C_{eo} \approx 500mg/dm^3$. It is seen in Fig. 5.19 that the fundamental difference in extraction behavior stems from the difference in the carrier type and the external phase pH.

LIX 84 I is a pure ketoxime that is moderately strong copper extractant but kinetically slow at 2 pH just 50% extraction of copper is registered, although its pH isotherm shows that at pH = 2 almost quantitative removal would be taking place. From the pH isotherms the pH_{50} is found 0.9, hence based on the considerations mentioned above at pH 2.4 quantitative removal is expected. Increasing the pH to 5 results in almost quantitative removal of copper.

LIX 84 is a mixture of 90 % ketoxime and 10% salicylaldoxime and has a faster kinetics in comparison to LIX 84 I due to the presence of strong copper extractant dodecyl salicylaldoxime. The performance of LIX 84 at pH of 1, 2 and 5 are shown in the Fig. 5.19. It is seen that at 1 pH LIX 84 performance is dismal with only 20 % removal of copper. The partition coefficient for copper at 1 pH between the organic and aqueous phase is just 1.83 for C_C = 10% . Increasing the pH to 2 results in a dramatic increase in the rates and extent of extraction leading to 98.6 % removal at 60 minutes. Further increasing pH to 5 results in quantitative removal (98.6 %) at 20 minutes. The relative increase in rates at each pH level in comparison with LIX 84 I is attributed to the presence of salicylaldoxime in the carrier.

LIX 984 NC is a mixture that contains 60% ketoxime and 40 % dodecyl salicylaldoxime. Further, it contains oximes in a more concentrated form the total oxime content in LIX 984 NC is 2.29 m against 1.5 M for the case of LIX 84 and LIX 84 I. The distribution coefficients obtained with these LIX reagents are listed below as a function of pH.

	K			
pH	1	1.5	2	5
LIX 84	1.83	26.08	152.2	613.62
LIX 984 NC	8.83	----	174.3	812.5

The performance of ELMs containing LIX 984 NC at pH = 1 is highly encouraging. Almost 80 % copper is recovered in 60 minutes. Moreover, the plateau in concentration was not arrived and more removal is expected at extended time periods. At higher pH values of 2 and 5 quantitative removal of copper is observed. The rates of removal using LIX 984 NC are faster than LIX 84 in all the situations however at pH = 5 the rates are nearly the same.

Results of a solo run performed at 2 pH with CYANEX 302 in the membrane phase of the ELMs keeping all other membrane and process parameters identical is seen in Fig 5.19. This run exhibits the highest initial rates in comparison to all other extractants, this is understandable since it is well established that acidic extractants display faster kinetics in comparison with the chelating extractants. The CYANEX reagents have not been employed for the extraction of copper in conventional solvent extraction mostly in view of their high viscosity and large reagent loss due to substantial solubility of these organophosphorous acids in water. These reagents offer potential opportunities for the extraction of copper and other metals using ELMs.

Fig. 5.20, shown below, shows the extraction behavior of copper at 1 pH with LIX 84 and LIX 984 NC using 1.5 M H_2SO_4 as the stripping phase, it also compares the effect of stripping phase acid concentration on the rates of extraction when all other parameters remain unchanged. It can be seen that increasing the acid phase concentration in the ELMs containing LIX 984 NC as carrier has not resulted in any significant difference in the amount extracted. This behavior is contrary to that observed in Fig. 5.12 for the extraction of copper using LIX 84, similar behavior was observed by Völkel *et al.* (1980) in their investigation on copper removal using LIX 64N.

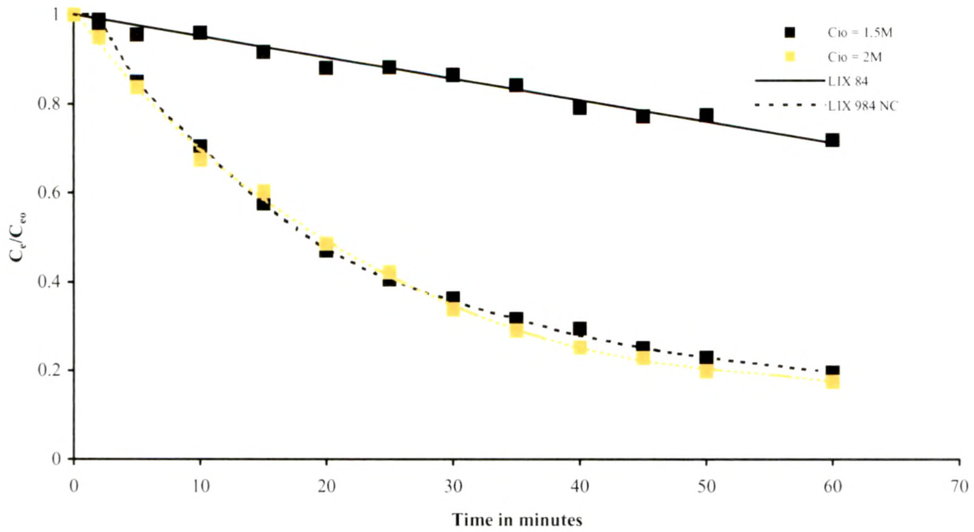

Fig. 5.20: Effect of C_{io} on extraction of copper from sulfate media at pH 1 using LIX 84 and LIX 984 NC

(N= 160rpm, $\phi = 0.5$, Span 80 = 3%, TR = 1:6, C_C = 10%, pH = 2)

5.6 EXTRACTION OF COPPER AND NICKEL FROM AMMONIACAL MEDIA USING ELMs

The chemistry of ammoniacal extraction of copper and nickel was briefly discussed in Section 5.2. Since copper and nickel occur adjacent on the periodic table, their chemistries are very similar. Further copper and cobalt are the base metals most commonly occurring with nickel in solution produced from the solubilization of nickel-containing material. In the past separations of these elements was mostly based on selective precipitation. The introduction of specific extractants has made this separation amenable by solvent extraction techniques.

It is possible to develop metal separation schemes by using the extraction isotherms and selectivity data. For example, the pH isotherms of LIX 84I with Cu (II) and Ni (II) suggest that good separation of Cu-Ni can be made with LIX 84 I by controlling the pH in the extraction stages of conventional solvent extraction. All the copper can be extracted at low pH (≈ 2) before the system is adjusted with ammonia to higher pH where the nickel is extracted. This type of scheme is used on a commercial scale at the S.E.C. Corporation in Texas for copper and nickel recovery from a refinery bleed stream (Ritcey, 1983)

The chemistry of nickel does not lend itself to the development of a nickel-selective extractant particularly in acid media. The rate of exchange of most ligands with nickel by displacing the inner hydration sheath of water molecules is well known to be kinetically far slower than complexation with other base metal cations. Except for ammonia – based systems, approaches to purifying nickel leach liquors have traditionally concentrated on the removal of the other elements from the nickel liquors (Sole and Cole 2002)

Copper is more strongly extracted from ammoniacal solution than is nickel using LIX 84 I. Thus copper nickel separations from ammonia leach solutions are possible using LIX 84 I. The problem however is to effectively use ELMs for such separations. Many operational difficulties are foreseen copper requires a relatively strong acid for stripping, whereas nickel requires weak acid. Further there is tendency for extraction to decrease with increasing ammonia concentration, this is explained by the extraction /stripping equation for a typical bivalent metal cation as shown for nickel in Eq. 5.8. In essence, the ammonia in solution functions as a coordinating ligand and competes with the organic extractant for the metal ion. The reaction is reversible and stripping with ammonia might be practical in some situations.

5.6.1 Extraction of nickel from ammoniacal media

To investigate the feasibility of nickel extraction from ammoniacal media using ELMs containing LIX 84 I as carrier, a number of trial runs were conducted at different pH values of the external phase ranging from 8 to 10. The pH extraction isotherms of LIX 84 I and other oximes suggests that stripping of nickel requires a weak acid typically having pH ranging from 2 to 3 (Ritcey 1983, Redbook 1997,2001, Sole and Cole 2002). Hence extraction using ELMs were carried out with dilute sulfuric acid in the inner phase having pH around 2. Further strong ammonia solutions in the internal phase were also tried for stripping of nickel. In all these runs the carrier concentration was 5 %, $\phi = 0.5$, $W_{surf} = 3$ %, N = 160 rpm, TR = 1:6 and $C_{eo} \approx 500$ mg/dm^3.

The ammoniacal feed solution was prepared by dissolving nickel sulfate in 5 % ammonium sulfate solution and pH adjusted to the desired value using ammonium hydroxide solution. Hardly 10 % removal of nickel was obtained in these trials. Stripping of nickel is problematic; it is well known that the kinetics of nickel stripping from oximes is slow relative to the rate of extraction (Sole and Cole 2002). It was concluded that these schemes though workable with conventional solvent extraction are not feasible with ELMs in view of the limited internal volume in ELMs to affect stripping low concentraton of stripping phase implies extremely low capacities. Moreover, having extraction and stripping in one stage inhibits the possibility of multistage stripping as prevalent in solvent extraction.

Parija *et al.* (1998) reported that in order to have near quantitative extraction of nickel in a single extraction stage using LIX 84 I as extractant it was essential to have an equilibrium pH around 8. Hence the pH of external solution was closely balanced near 8. Further, to enhance the capacity of the ELMs for extraction and stripping, the carrier concentration C_C was increased to 10 % LIX 84 I, and the internal phase acid concentration C_{io} was increased to 1.5 M. The reason for increasing C_{io} was also influenced by the idea that copper stripping would require acid of identical concentration. In case nickel did not get significantly stripped under these conditions then nickel contamination in the stripping phase during extraction of copper – nickel mixtures could be ruled out.

Experiments were conducted with external phase pH balanced at 8.1 and also at 9.1 for comparison of extraction performance. The other membrane and process parameters were held constant with $C_C = 10$ % LIX 84 I, $\phi = 0.5$, $W_{surf} = 3$ %, TR = 1:6, N = 160 rpm and $C_{eo} \approx 500$ mg/dm^3. The results are reported in Fig. 5.21. It is seen that at pH 8.1 almost 50 % of nickel is extracted between 6 to 8 minutes. With pH 9.1 the extraction is inferior and only 30 % extraction is recorded. Membrane breakage is observed in the case of pH 8.1, although membrane breakage is not visible in terms of concentration changes at pH 9.1 but there was substantial reduction in emulsion volume indicating membrane breakage in this case. It could so happen that the continual increase in extraction recorded was taking place only in the organic phase.

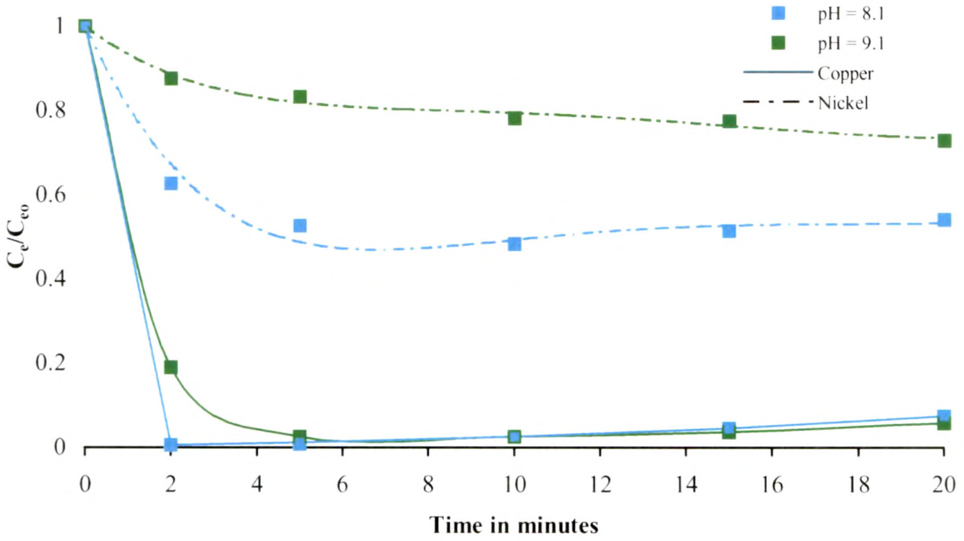

Fig. 5.21: Effect of pH on extraction of copper and nickel from ammoniacal media using LIX 84I

(N= 160rpm, $\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5M$, TR = 1:6, $C_C = 10\%$)

This observation prompted solvent extraction investigations, under identical process conditions, keeping the volume of organic phase in the system equal to the volume of organic phase in ELMs added in the above runs. The LIX 84 I concentration in the organic phase was 10 % (vol). The nickel loading observed in these experiments was 56 % at pH 8.1 and 51 % at a pH of 9.1. The final pH was 8.06 and 8.99 respectively. Thus it was concluded that almost no stripping had taken place in the earlier experiments using ELMs, and the nickel extracted in these experiments as seen in Fig. 5.21 resided in the membrane phase. Evidence for this was obtained when the emulsion used for the extraction of nickel split to its components. It was observed that the oil phase was green in color like the loaded membrane of solvent extraction studies and analysis of the aqueous phase did not show the presence of nickel in it.

5.6.2 Extraction of copper and nickel from ammoniacal media

Results of copper extraction from ammoniacal media using ELMs containing LIX 84 I as carrier at pH of 8.1 and 9.1 are also shown in Fig. 5.21. The membrane composition was exactly identical to that used for nickel studies, other operating conditions including feed preparation were also identical to the previous experimental conditions for nickel extraction.

It can be seen from Fig. 5.21 that quantitative removal of copper was obtained in 2 minutes when pH was 8.1. The pH of the extraction system showed sharp decrease with time. At duration of 2 minutes the pH was 8.1, at 5 minutes it was 7.5 and at 10 minutes 6.5. After 60 minutes the pH was 2.2. This indicates that during the actual time frame of extraction there was no membrane breakage. However membrane breakage sets in just few minutes and is very severe after about 30 minutes.

Extraction of mixture of copper and nickel from ammoniacal media using ELMs were investigated with LIX 84 I as the carrier the emulsions had $C_C = 10$ % LIX 84 I, $\phi = 0.5$, $W_{surf} = 3$ %, TR = 1:6, N = 160 rpm and the concentration of each solute was about 500 mg/dm^3. Feed was prepared in an identical manner to that discussed above. Fig. 5.22 shows the extraction behaviour of this system. Copper gets quantitatively extracted in just 2 minutes of the run while nickel behaves in the same pattern as observed earlier. The separation factor at 5 minutes turns out to be 99.89.

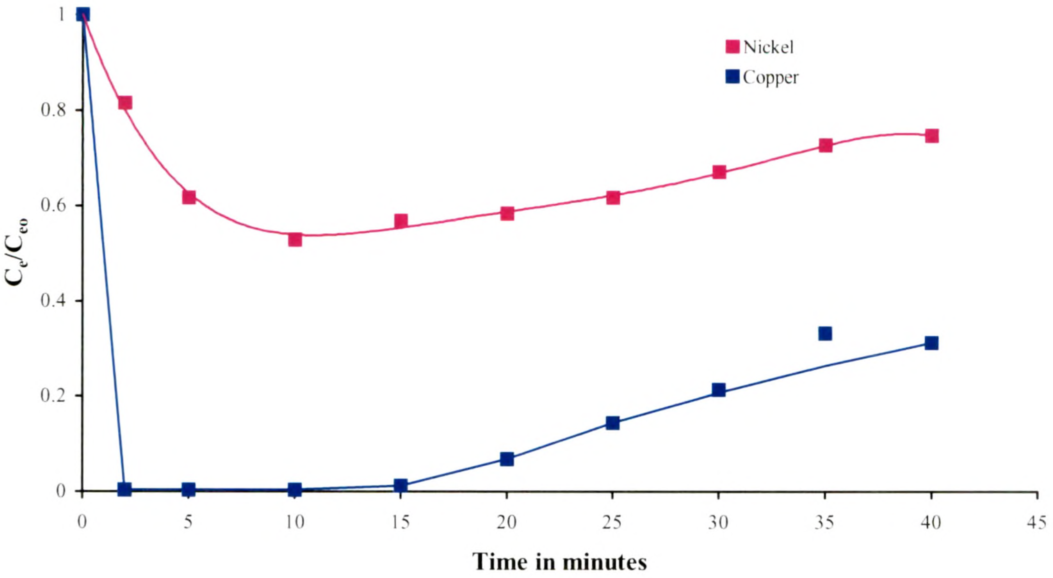

Fig. 5.22 Simultaneous extraction of copper and nickel from ammoniacal media using LIX 84I

(N= 160rpm, $\phi = 0.5$, Span 80 = 3%, $C_{io} = 1.5M$, TR = 1:6, $C_C = 10\%$)

It may be concluded that separation of copper and nickel using chelating extractants in ammoniacal media may not be a good idea. Separations of such mixtures are more conveniently achieved in acidic media, at pH ≈ 2, where nickel is not loaded and copper could be quantitatively removed.

5.7 FEATURES OF EMULSION SWELLING AND BREAKAGE

Emulsion swelling was measured after each run; there was considerable swelling at the end of the run in comparison to the case of extraction of phenols. However in case of metal extractions the run durations were of 1 hour while in case of phenols they were just half an hour. It was interesting to note that in the first half hour of the runs when most of the extraction took place there was very little swelling around 5 % while in the later half hour of the run swelling was substantial. Swelling could be largely attributed to osmotic flow due to the high acid concentration in the inner phase of the membrane. The' was no difference in the amount of emulsion swelling with carrier type. Table 5.1 details the swelling behavior of W/O emulsions used for metal extractions

Table 5.1: Swelling of W/O emulsions with acid in internal phase

Parameters					Swelling % at N = 160 rpm
Time Min.	C_C %	TR	ϕ	Cio M	
30	10	1:6	0.5	1.5	4.76
60	5	1:6	0.5	1.5	13.04
60	7.5	1:6	0.5	1.5	28.57
60	10	1:6	0.5	1.5	28.57
60	15	1:6	0.5	1.5	25.93
60	20	1:6	0.5	1.5	25.93
60	10	1:6	0.4	1.0	28.57
60	10	1:6	0.6	1.0	20.00
60	10	1:6	0.5	2.0	28.57
60	10	1:4	0.5	1.5	40.47
60	10	1:10	0.5	1.5	23.07
60	10	1:6	0.5	1.0	28.57
60	10	1:6	0.5	1.0	34.21 at N= 190 rpm

No severe membrane breakage was observed except in the extractions from ammoniacal media. On the whole the membranes were very stable in comparison with the membranes formulated for extraction of phenols using NaOH solutions in the inner phase. It is felt that W/O emulsions formulated with Span 80 as the emulsifier are inherently unstable in alkaline environments.

5.8 SUMMARY

The extraction of copper and nickel was investigated using chelating LIX reagents as carrier in the membrane phase. The effect of type of extractant, its concentration, various membrane parameters such as internal phase reagent concentration, internal phase volume also the process parameters such as Treat ratio, stirring speed, the external phase concentration and the external phase pH were considered. It could be inferred that the external phase pH is the dominant parameter to affect separations the selection of pH is specific to the type and nature of extractants.

Three chelating extractants LIX 84 I, LIX 84 and LIX 984 were used to extract copper from sulfate media at pH = 2 and pH =5. These three extractants inherently differ from each other with respect to the amount of dodecylsalicylaldoxime present in them, greater the amount of the salicylaldoxime, greater is the efficiency of the extractant for copper removal. Quantitative extraction of copper was observed at pH = 5 with LIX 84 and LIX 984 NC. However at pH =1, LIX 84 performed rather poorly while LIX 984 NC did not show any significant decline in performance. Thus LIX 984 NC is strongly recommended for extractions at low pH. The monothio phosphinic acid CYANEX 302 gave nearly quantitative removal of copper at pH =2, it would be worthwhile to study the extraction of copper and other bivalent metals using CYANEX 302.

Extraction of copper and nickel from ammoniacal media shows very different behavior in comparison with extraction from acidic media. Extraction of copper using LIX 84 I was very rapid and quantitative at pH = 8.1. It was observed that under these conditions nickel got loaded in the membrane phase but could not be stripped. Swelling was quite severe in all experiments due to osmotic pressure gradients but membrane breakage / leakage was not observed in any case other than extraction from ammoniacal media. It appears that Span 80 stabilized membranes are not stable under alkaline conditions.