

Removal of Sulphuric Acid from Electrowin Solutions by Reactive Extraction Using Alamine 336 in Isodecanol-Shell sol 2325 Solvent Mixture

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Abstract: The removal of sulphuric acid from electrowin solutions from tank houses of mining operations by reactive extraction using alamine 336, isodecanol and shell sol 2325 solvent mixture was studied with a view to evaluating the effectiveness of alamine 336 and isodecanol-shell sol 2325 solvent as carriers of the acid. Other efficiency evaluations were carried out using distilled water and sodium carbonate as strippers of the acid, aqueous/organic and organic/aqueous ratio and number of stages in a three stage extraction plant. The results showed that isodecanol-shell sol 2325 system was effective in carrying the acid with efficiencies reaching 52 % when the acid was stripped with distilled water at aqueous/organic ratio of 15:1, 99 % when stripped with sodium carbonate at aqueous/organic ratio of 5:1, 99 % when extracting with alamine 336 in isodecanol-shell sol 2325 at organic/aqueous ratio of 2.5:1 and 93 % for the third stage in a three-stage extraction unit at organic/aqueous ratio of 2:1. Therefore the system alamine-isodecanol-shell sol 2325 was effective in removing sulphuric acid from electrowin solutions.

Keywords: Sulphuric-acid; Reactive-extraction; Three-stage; Alamine-336; Optimum-conditions, Shell sol 2325; Hydrometallurgy; Chemical-technology.

Introduction

The extraction of sulphuric acid (H_2SO_4) from electrowin solutions was studied at constant temperature and pressure though most extraction processes depend on the nature of extraction process, the temperature, pH and residence time which could have some effect on the yield and selectivity of the extractant^{1,2}. Atmospheric pressure has little effect on extraction unless governed by vapour pressure conditions^{3,4}. Temperature can be used to alter the selectivity, extraction rate and to keep the viscosity low thereby minimizing mass transfer resistance^{5,2}. The pH is used to maintain the distribution coefficient and minimize degradation of solvent and product⁶. Residence time is an important element in reactive extractions such as that in metal separations^{7,8}.

The H_2SO_4 can be extracted from electrowin solutions, using the extractant (amine 336) and a modifier (isodecanol) in a diluent (shell-sol 2325). This type of solvent combination was different from combinations used in studies elsewhere⁹. The use of shell sol 2325 has not been reported in H_2SO_4 extractions. Extractants such as alamine 336, D2EPHA and TBP and modifiers such as isodecanol and solvesso 150 are used to increase solubility in o-phase and modify equilibrium^{10, 11, 12}. Diluents are used to decrease viscosity and modify the density or alter the loading capacity of the o-phase e.g. shell-sol or kerosene^{13, 14, 15}.

Electrowin solutions have been reported to damage the environment because of the H_2SO_4 , which is a strong oxidant and is reported to kill life forms in water and soils^{16, 17}. One of the ways in which the acid can be removed from electrowin solutions is by neutralisation with alkaline compounds; sodium carbonate (Na_2CO_3), water (H_2O) and sodium and ammonium hydroxides ($NaOH$; NH_4OH)¹⁸. Beneficial production of H_2SO_4 , sodium sulphate (Na_2SO_4) and ammonium sulphate ($(NH_4)_2SO_4$) can be achieved through this method in order to support different processes and make the environment sustainable⁹.

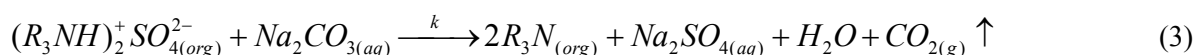
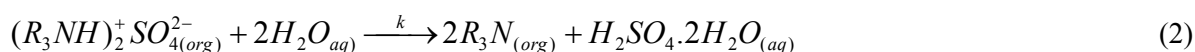
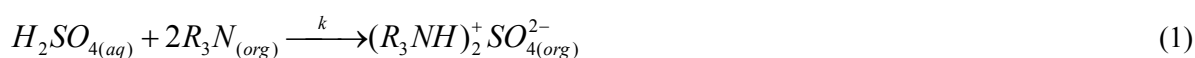
The best way to evaluate the performance of extraction process is to determine the efficiency¹⁹. This can be carried out at different levels of concentration of extractant, acid/organic ratio and number of extraction stages^{20, 21, 2, 9}. By comparing the acid-loading capacity of alamine 336 to the stripping capacity of H_2O and Na_2CO_3 it is possible to determine the optimum conditions for the process. The overall objective of the study was to establish the optimum performance of alamine 336 in isodecanol-shell sol 2325 solvent for the recovery of H_2SO_4 from electrowin solutions from tank houses with the specific objectives of determining the optimum concentration of alamine 336 to extract H_2SO_4 , the maximum loading capacity of alamine and the optimum phase ratios for acid recovery.

Principles of Extraction

The reactive extraction can be carried out in stirred batch, series or continuous counter-current systems^{22, 23}. The reaction rate between the amine and H_2SO_4 is dependent on the level of concentration of reactants, temperature, ratio of acid to organic or organic to acid and the number of stages²⁴.

When the amine (R_3N) reacts with H_2SO_4 , an intermediate-complex compound ($R_3NH_2SO_4$) is formed as given by equation (1), which reacts with alkaline compounds, in order to regenerate the amine to form more-stable and less-acidic compounds such as water (H_2O) and salt (Na_2SO_4) and carbon dioxide (CO_2) as given by equations (2-3). These reactions can be by ion exchange, ion pair extraction or solvation mechanisms.^{25, 26, 27, 28}

The rate of reaction during extraction is dependent on the concentrations of reactants and products as given by equation (4) where k_1 and k_2 (s^{-1}) are constants for the forward and reverse ionisation of the amine while k_3 (s^{-1}) is the reaction constant of amine and acid to form the amine-acid complex (AB). The symbols R_{AB} , C_A and C_B are the reaction rate ($mols^{-1}$), concentration (mol/L) of acid and amine respectively. The conversion (dN_A) and efficiency (Eff) of extraction and regeneration of alamine 336 can be given by equations (5-6), for batch and flow systems where N_{A0} and N_A represent the number of moles available initially and after reaction, N_{AB} (mol/L), N_{BR} (mol/L), k_a (s^{-1}) and V_r (m^3) represent amounts of amine complex produced, acid in raffinate and volume of reactor respectively while K is the equilibrium constant, F_{A0} and F_A ($g/minute$) and t (s) represent the initial and final flow of acid in the reactors and the reaction time respectively^{22, 23}.



$$R_{AB} = \frac{(k_1 k_3 / k_2) C_A C_B^2}{1 + (k_3 / k_2) C_A} \quad (4)$$

$$dN_A = -\frac{k_a}{V_r} \left\{ N_A N_{BR} - \frac{N_{AB}}{K} \right\} dt \quad (5)$$

$$Eff = (F_{A0} - F_A) / F_{A0} = (N_{A0} - N_A) / N_{A0} \quad (6)$$

Equipment, materials and Methods

Equipment

A number of equipment was used during the study. A stop watch was used to measure the time, the pH meter was used to measure the pH of solutions, a stirrer was used to agitate and homogenize the solutions, measuring cylinder was used to measure the volume of samples, a hot plate was used to heat liquors, a beaker was used for storage, heating and collecting solutions, a separating funnel was used to disengage the phases, thermometer was used to measure the temperature, a pipette was used to measure the volumes of samples and filtration equipment was used to remove suspended solids from solutions.

Materials

Organic solvent comprising different concentrations of alamine 336, Shell-sol 2325 and isodecanol was used as extractant. Alamine 336 was used as extractant responsible for the transfer of solute from the aqueous to organic layer. Shellsol 2325 was used as diluent in which extractants may be dissolved to form organic phase. The iso-decanol was used as a phase modifier to improve the properties such solubility of extractant or interfacial properties. Samples collected from electrowin solutions of cobalt and copper tank houses. Sodium carbonate (Na_2CO_3) was used to titrate with the acid-loaded organic in order to assess the level of H_2SO_4 recovered.

Methods

Maximum loading capacity of alamine 336

A 50 mL aliquot of alamine 336 was equilibrated with 50 mL copper electrowin spent electrolyte solution

containing 33.6 g/L H_2SO_4 for 3 minutes at 25°C. The aqueous phase was rejected after the phases separated. A fresh solution of electrowin spent electrolyte was added to the partially loaded o-phase and the extraction was repeated a number of times. A 5 mL aliquot of loaded o-phase was titrated against 0.1 M Na_2CO_3 to determine the acid content and generate a sample for metal analysis. This was done at different o-phase strengths.

Optimisation of alamine 336 for acid loading

In order to determine the optimum level of alamine 336 for acid extraction, the o-phase-amine solution was prepared in strengths of 15, 20, 25, 30, 35, and 40 % (Table 1). A series of single-stage contacting tests were carried out at the various alamine 336 concentrations at temperatures of 20-27 °C. The resulting aqueous solution was analysed for acid content in order to establish levels of the acid in the o-phase.

Acid extraction at different stages and varying O/A ratios

The bench counter-current extraction was conducted at O/A ratios of 1:1, 1.5:1 and 2:1 (Figure 2 (a), (b) and (c)). The extraction was carried out using regenerated 25 % alamine 336 in order to determine the efficiency. The organic regeneration was accomplished by stripping the previously loaded 25 % alamine 336 with 0.1M Na_2CO_3 solution at 50 °C. Thus, warm water was necessary in order to reduce the viscosity of the solvent.

Table: 1 Preparation of alamine-isodecanol-shell-sol reagents

No	Alamine (mL)	Isodecanol (mL)	Shell-sol 2325 (mL)	Concentration (%)
1	15	15	70	15
2	20	20	60	20
3	25	25	50	25
4	30	30	40	30
5	35	35	30	35
6	40	40	20	40

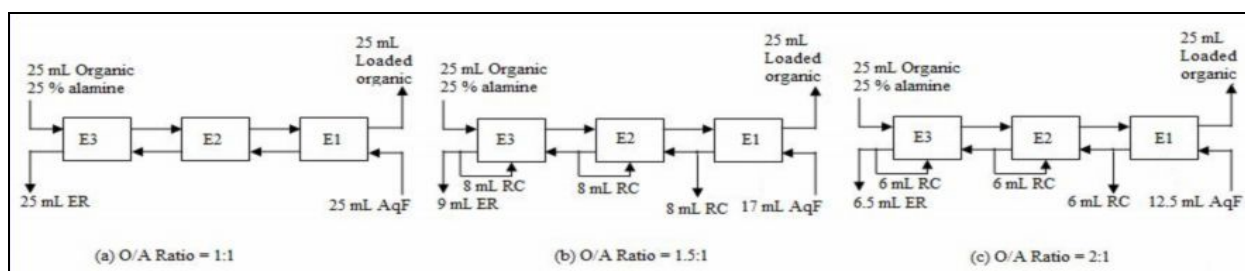


Figure 1 The three stage extraction plant with recycle at different O/A ratios

Acid stripping using water and sodium carbonate

The stripping of organic was conducted at A/O ratios of 1:1, 2.5, 5:1, 10:1, and 15:1, initially using distilled water at pH6.5 followed by 0.1M Na₂CO₃. This was carried out using loaded 25 % alamine 336 in o-phase in order to determine the effect of O/A ratios and stripping solvent on the stripping efficiency.

Data analysis

The data was analysed in excel and SPSS soft ware using exploration method in order to establish the underlying trends of data that would establish the relationship between the dependent and independent variables^{29, 30}.

Results

Loading capacity of alamine 336

The loading capacity of alamine can be seen in Table: 2. The increase in alamine concentration produced an increase in the phase-separation period. Though there

was an increase in the acid load in the o-phase as a result of this effect, there was little effect on the loading capacity, which was found to be at an average of 141 g/L. The loading capacity, therefore, was characteristic of the type of extractant and the environment in which it is placed.

Effect of distilled water on acid extraction

The stripping of the H₂SO₄ using distilled water produced and increase in efficiency (Eff) of 36 % from 16 to 52 % when the aqueous/organic ratio increased from 1 to 15 at constant volume of o-phase (V_{org}) of 25 ml and varying volume of aqueous (V_{aq}) (Figure 2). This increase produced a decrease in acid raffinate solution (AR) from 12 to 2 g/L. Therefore, increasing the aqueous/organic ratio increased the extraction of acid from the amine-acid complex. The acid produced can either be recycled to reduce the cost of fresh acid usage or sold to after purification in order to defray expenses.

Table: 2 Composition of loaded organic

Alamine concentration (1)	Phase separation period	Concentration of H ₂ SO ₄ (2)	Loading capacity (2/1)
vol %	seconds	g/L	g/L
15	10	20.2	135
20	30	28.0	140
25	40	36.5	145
30	240	42.7	142

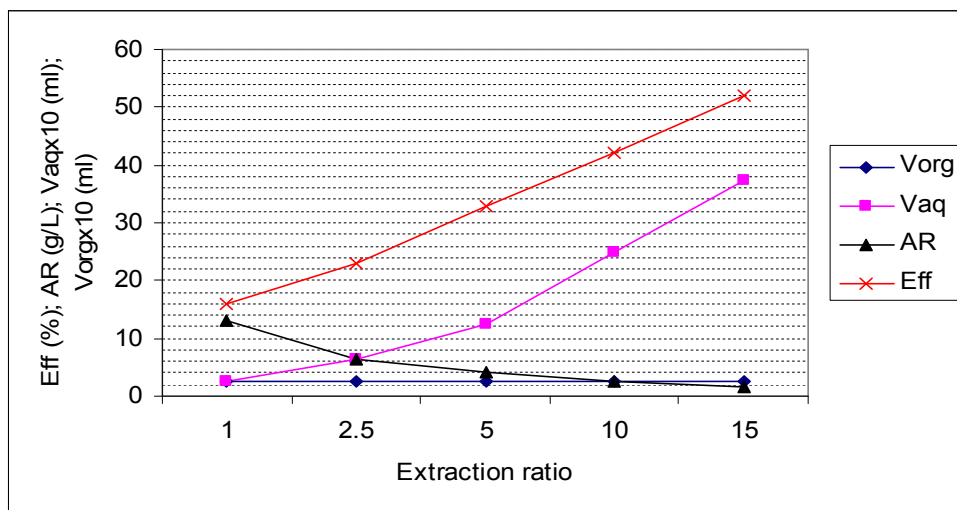


Figure 2 Effect of acid/organic ratio on the extraction efficiency using water

Effect of sodium carbonate on acid extraction

When the volume of o-phase, containing stripping agent (Na_2CO_3) at pH 10.74, was kept constant at 25 ml while that of the a-phase increased from 25 to 380 ml, the extraction efficiency (Eff) increased from 54 to 99 %, i.e., the level of the acid in o-phase increased (Figure 3). The amount of acid in the raffinate (AR) decreased correspondingly from 32 to 2 g/L. Therefore, increasing the aqueous/organic ratio improved the recovery of acid using Na_2CO_3 as extractant reaching maximum efficiency at aqueous/organic ratio of 5:1.

Effect of alamine 336 on acid extraction

The results in Figure 4 show that the extraction efficiency (Eff) of H_2SO_4 increased from 42 to 94 % when the concentration of alamine 336 increased from 15 to 40 % at organic/aqueous ratio of 1.5:1. This was attributed to the increase in acid (Ac) in the o-phase due to the reaction with alamine 336. At the same time, the acid in raffinate (AR) decreased from 20 to 1 g/L. It was observed, therefore, that alamine 336 is a potent extractant of acids. However, its effect on the extraction of nickel (Ni) was small when compared to that of extracting H_2SO_4 . Such potential can be advantageously used to clean-up acids in effluents that would be a risk to life in the environment.

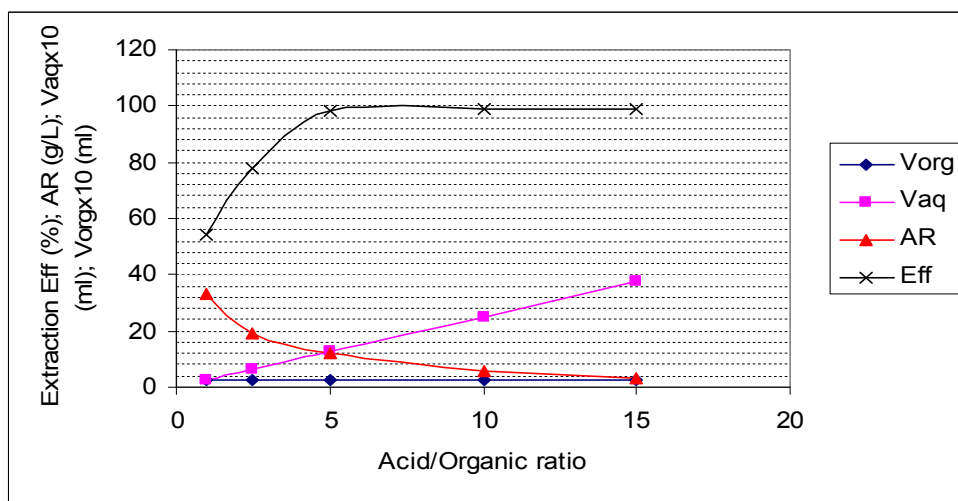


Figure 3 Effect of Aqueous/Organic ratio on the extraction efficiency using Na_2CO_3

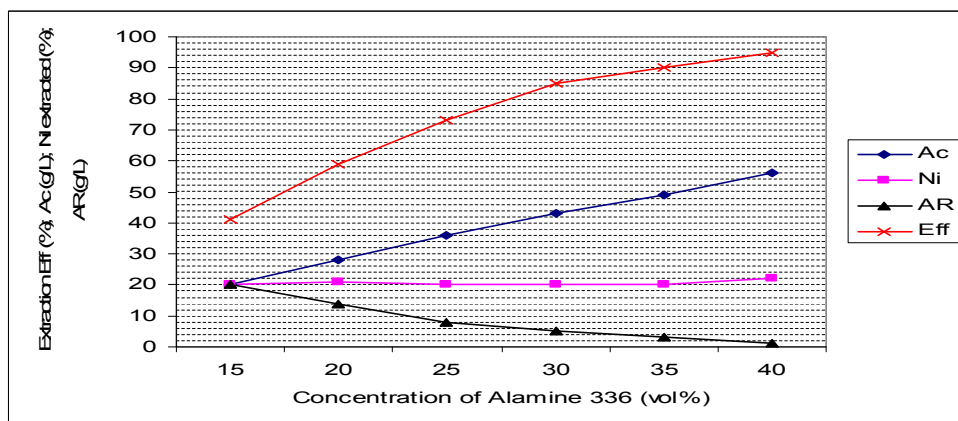


Figure 4 Effect of alamine 336 concentration on acid extraction

Effect of organic/aqueous ratio on acid extraction

In order to investigate the effect of organic/aqueous ratios on the extraction of H₂SO₄, the volume (mL) of aqueous (V_{aq}) was kept constant while the volume (mL) of organic (V_{org}) varied to give the organic/aqueous ratio range of 1:1-15:1 at alamine concentration of 25%. The results in Figure 5 show the increase in acid extraction (AcLoad) reaching 99% efficiency at organic/acid ratio of 2.5:1. Further increase in the ratio did not increase or decrease the extraction efficiency. The acid content in the aqueous (AcAq and AcAqq) decreased while that in the o-phase (AcOrg and AcOrgg) increased reaching maximum at organic/aqueous ratio of 2.5:1. Further increase in the ratio did not increase the acid content in the o-phase.

Effect of number of stages on acid extraction

The effect of the number of stages on the extraction of H₂SO₄ was conducted at 20-27 °C using three stages at

different organic/aqueous ratios (R) at 25 % concentration of alamine. The results in Figure 6 indicate that the Eff (%) was highest (93 %) at R of 2:1 and lowest at R of 1:1 (60 %). In stage 2 the highest efficiency was that at R of 2:1 (75 %) while the lowest was that at R of 1:1 (12.5 %). In stage 1, the highest Eff (%) was at R of 2:1 (20 %) while the lowest value was at R of 1:1 (5 %). The acid level in raffinate (AR) was lowest in stage 3 (5 g/L) while the highest value was that at R of 1:1 (20 g/L). The results demonstrated that the increase in the number of stages produced an increase in the H₂SO₄ extraction at any level of alamine concentration. If the extraction could reach 93 % level, it means that most acids of this type, coming out of industries with process waters, would be effectively removed to allow for low cost neutralization that would make the environment sustainable.

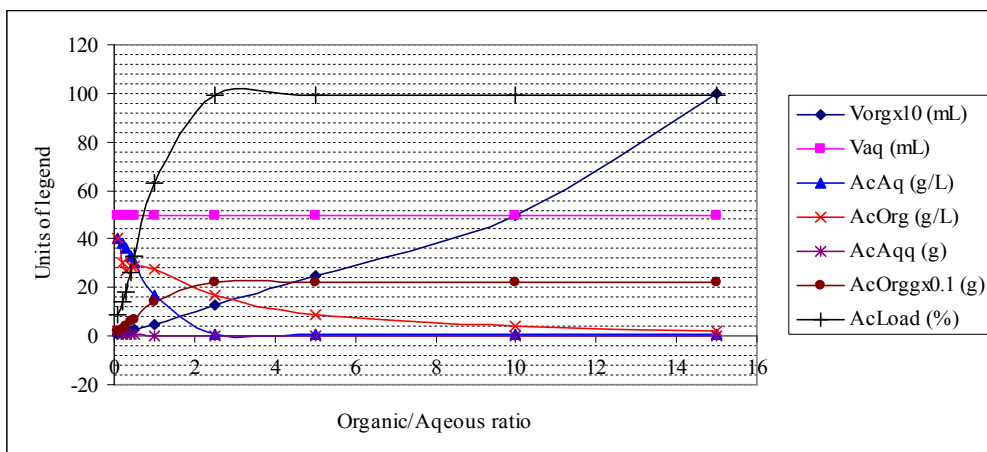


Figure 5 Effect of organic/aqueous ratio on the extraction of acid

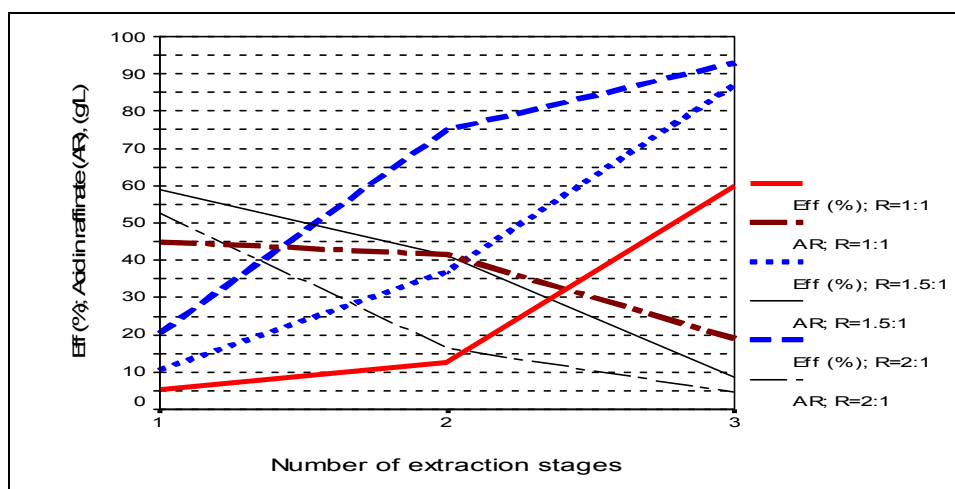


Figure 6 Effect of number of stages on the extraction of acid

Discussion

Water was found to be a poor stripper of H_2SO_4 as evidenced by the results obtained in this study and studies elsewhere²¹. Even at the acid/organic ratio of 15:1, the efficiency just reached 52%. However, this would be one of the best ways to recover the acid from the o-phase and recycle it to reduce costs or sale it in order to sustain the process. On the other hand, sodium carbonate was a powerful stripper of the acid with efficiency reaching 99% at extraction ratio of 5:1. Thus, Na_2CO_3 , like other acid neutralizers, such as lime and sodium hydroxide, would be the best choice to remove the acid from acid-loaded effluents from mining and other chemical industries in order to prevent the catastrophic fate of life forms in water and environment. The use of alamine 336 in the system alamine-isodecanol-shell sol 2325 presented an alternative means of recovering the H_2SO_4 from industrial effluents if the damage that can be caused to water and environment either by the acid and alkaline compounds is to be avoided³¹. Various studies have used alamine 336 as complexing agent enroute to extraction of acids and metals from different combinations of solvents^{20, 13, 21, 32, 33}. The advantage of using isodecanol and shell-soll 2325 with alamine is that these organic chemicals can be collected and properly disposed leaving the effluents risk free before discharging into water and environment. Thus the risk to fish and other life forms in water and environment can be reduced¹⁷. Isodecanol as modifier performed well in shell sol 2325 though poor performance has been reported elsewhere⁹.

The increase in aqueous/organic ratio or organic/aqueous ratio produced an increase in efficiency particularly the organic/aqueous ratios which gave higher values (99%) at 25% alamine concentration and ratio of 2.5:1 and 93% at a ratio of 2:1 when compared to values of stripping with water which gave 23 % at a ratio of 2.5:1 and 78% when stripped with Na_2CO_3 extractant or stripper. The recovery of acid with increased volume of o-phase provided extra room for alamine to transport H_2SO_4 into the o-phase. Whilst the optimum ratio when stripping with water was >15:1, that for sodium carbonate was lower (5:1) while that for alamine 336 was lowest (2.5:1). This meant that the use of organic/aqueous layer was more efficient than that of aqueous/organic ratio and alamine required a lower optimum ratio.

Though the McCabe and Thiele method provides the best way to determining the number of stages required for the extraction as demonstrated by studies elsewhere³⁴, the method used in this study can equally be used to determine the number of stages required at the point where the efficiency is considered the

highest. It was noted that the increase in the number of stages increased the extraction efficiency because the efficiency in the first stage was lowest at 20 %) while that in the second stage was higher at 75 %) and that in the third stage was highest at 93 % level using an organic/aqueous ratio of 2:1. These values were in agreement with the discussion in Levenspiel (1962). Thus a three stage counter-current system could be economical when compared to a system with more than three stages.

The efficiency produced by alamine-isodecanol-shellsol 2325 system in three stages was higher (99%) than the efficiencies of other systems. For example, aliphatic tertiary amine tris(2-ethylhexyl)amine (TEHA) as the extractant, Shellsol 2046 as diluent and octanol as a modifier produced an efficiency of 90 %^{35, 36}, TEHA in octanol produced an efficiency of 85% in four stages³⁴, TEHA in kerosene produced an efficiency of 94 % at acid/organic ratio of 5:1 with stripping efficiency ranging from 94.8-99.7 %³⁷, Cyanex 923 in octanol produced an efficiency of 95% in five stages³⁴, LIX 622 in SX-1 produced an efficiency of 97-98%⁸, alamine 308 in isodecanol produced an efficiency of 90-98 %^{38, 9}.

Conclusion

The recovery of H_2SO_4 could not be efficiently achieved using distilled water and therefore water was found to be a poor agent to recover H_2SO_4 from acidic-industrial effluents. However Na_2CO_3 was found to be the best agent to remove the acid from effluents at low aqueous/organic ratios but has demerits of killing fish and other life forms in water and environment.

The alamine336-isodecanol-shellsoll 2325 system was found to be effective in recovering H_2SO_4 from industrial effluents at increasing concentrations of alamine with efficiencies reaching 99% at lower values (2.5:1) of organic/aqueous ratios.

The increase in the number of stages produced an increase in the extraction efficiency of H_2SO_4 with efficiencies reaching 93 % in the third stage at organic/aqueous ratio of 2:1. Thus alamine 336 was effective at a concentration of 25%.

Acknowledgment

I thank Chambishi Metals Plc who provided the equipment and materials for the study at their premises. I also thank Marvin Mumba who assisted in the handling, preparation and test run of the equipment, sample collection and evaluation of concentrations.

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