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EXTRACTION AND PRECIPITATION CHEMISTRY FOR MERCURY RECOVERY FROM AQUEOUS WASTES

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ABSTRACT

This paper describes an extraction-precipitation process to recover mercuric chloride from aqueous solutions. The process is a modification of a dicarboxylic acid recovery process that exploits the enhanced solubility of mercuric chloride in organic solvents loaded with water. Mercuric chloride in ethyl acetate has a solubility enhancement of 1.34 moles mercuric chloride per mole of water added to the solvent, consistent with previously reported phase behavior. Solubility enhancement is also reported for formates, in contrast to previously reported results. For example, propyl formate showed 2.91 moles mercuric chloride per mole water enhancement.

The modified process described in this paper relies on (1) favorable liquid-liquid equilibrium (mercuric chloride distribution into ethyl acetate or into propyl formate), (2) favorable liquid-solid equilibrium with enhanced solute solubility on addition of a minor constituent (water), and (3) preferential vaporization of the minor constituent from the solid slurry (relative volatility of water in mercuric chloride loaded ethyl acetate is four). Enhanced solubilities for zinc(II) chloride(3.46) and mercury(II) iodide(1.10) in isopentyl acetate indicate a potential application of the process for the recovery of other metal halides from aqueous wastes.

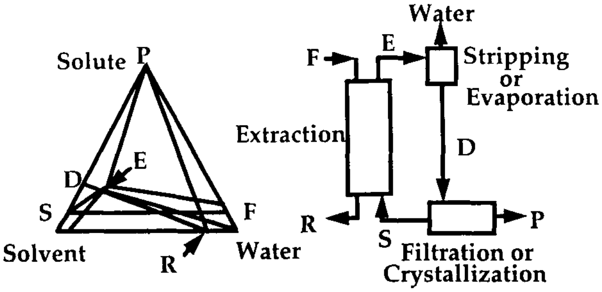
INTRODUCTION

The South Carolina Department of Health and Environmental Control (SCDHEC) reports that mercury-laden waste generation in the state approached 10 million pounds in 1990[1]. This figure does not include the mercury contribution from the F and H area seepage basins at the Savannah River Site (SRS) in Aiken, South Carolina, and is 26 times higher than that generated in the state of South Carolina in 1985. These mercury wastes include: battery mercury, wastewater sludges, lab packs, oxidizers, waste photographic chemicals, paint pigments, and some liquid mercury. A portion of the wastes are mercuric chloride. This paper presents a mercuric chloride recovery process that can be used to recover mercuric chloride from industrial wastes.

Alternative conventional mercury treatment technologies include[2,3]: sulfate or hydrazine precipitation, carbon adsorption, ion exchange, cementation[4,5], and roasting or retorting. Only roasting or retorting recovers pure mercury directly. The other methods involve an additional purification step for complete recovery, and all generate secondary wastes. The process reported here recovers pure mercuric chloride and generates no secondary waste.

Ion exchange, carbon adsorption[6], and solvent extraction[7] are economical alternatives for mercury(II) recovery. Solvent extraction of mercury(II) was investigated using various extractants, including: trioctyl phosphine oxide (TOPO)[8,9], tributyl phosphate (TBP)[9], trioctyl amine (TOA)[10], Aliquat 336 (a quaternary ammonium extractant)[11,12], oleic acid[13], sulfur based extractants[14,15,16,17] thiourea based extractants[18], and TRUEX process solvent (CMPO and TBP in n-dodecane)[19,20]. Extractants containing O or N as donor atoms show poor selectivity for mercury(II) compared to other metals[8]. Extractants containing sulfur as a donor atom have shown better selectivity for mercury(II)[14,15,16,17]. All these extractants recover mercury(II) as a solvent-metal complex.

Certain classes of solvents can recover mercuric chloride ($HgCl_2$) as a covalently bonded mercury complex, containing no extractant, from aqueous waste streams. Mercuric chloride shows enhanced solubility in these "wet" solvents. In other words, the addition of water to the solvent-solute binary significantly enhances the solubility of the mercuric chloride solute. Starr and King[21] invented a three-step process for recovering a pure solute from systems exhibiting enhanced solubility (Figure 1). This process recovers the pure solute and recycles the loaded solvent. This paper reports liquid-liquid and liquid-solid equilibria for solvent-solute combinations of Group 12(IIB) metal halides that show enhanced solubility and meet the criteria needed for a Starr-King process. This paper also reports the first application of the Starr-King process for an



F - Feed
E - Extract
R - Raffinate
D - Water Depleted Stream
P - Product
S - Solvent Recycle

FIGURE 1. Three-step solute recovery process flowsheet.

inorganic solute, $HgCl_2$. It further reports the first material balance and a modified design of a Starr-King process.

EXPERIMENTAL LIQUID-LIQUID AND LIQUID-SOLID EQUILIBRIA

Liquid-Solid Equilibria

Figure 1 includes an example ternary diagram illustrating solubility enhancement. A.W. Francis[22,23] published 154 ternary diagrams for Group 12(IIB) metal nitrates and chlorides. Solvent classes exhibiting enhanced solubility of mercuric chloride in a "wet" solvent included acetates, formates, and nitriles. Francis reported no specific solubility data other than a rough ternary diagram, so Francis' findings were verified in this paper. The liquid-solid equilibria experimental matrix is shown in Table 1. The solvents are similar to those used by Francis[22,23] and additional Group 12(IIB) metal solutes, other than mercuric chloride, are included. Tables 2-4 show specific solubilities observed and the extent of any solubility enhancement for zinc chloride, mercuric chloride and mercuric iodide in some representative solvents.

The effect of water on the liquid-solid phase envelope is shown graphically in Figures 2 and 3. These are plots of the liquid phase envelope on the solvent-rich side of the ternary

Table 1. SOLUTE-SOLVENT PAIRS FOR AQUEOUS TERNARY SYSTEMS EVALUATED IN THIS WORK.

Solvents	Solutes						
	zinc chloride	cadmium chloride	mercuric chloride	mercuric bromide	mercuric iodide	mercuric acetate	diphenyl mercury
acetates:							
methyl	X	X	X	X	X	X	X
ethyl	X	X	X	X	X	X	X
n-propyl	X	X	X	X	X	X	X
n-butyl	X	X	X	X	X	X	X
sec-butyl				X	X		
isopentyl	X	X	X	X	X	X	X
formates:							
methyl	X	X	X			X	X
ethyl	X	X	X			X	X
n-propyl	X	X	X			X	X
n-butyl	X	X	X			X	X
nitriles:							
3,3'-oxy dipropio			X				
3,3'-imino dipropio			X	X	X		

Table 2. $ZnCl_2$ SOLUBILITY AND SOLUBILITY ENHANCEMENT.

Solvent	$ZnCl_2$ Solubility (mol solute/mol solvent)	Observed Enhancement ($\text{solubility}/\text{solubility}_o$)
methyl acetate	0.488	NO
ethyl acetate	0.559	NO
n-propyl acetate	0.585	NO
n-butyl acetate	0.649	NO
isopentyl acetate	0.730	3.46
water[24]	0.573	

NO = no enhancement observed

Table 3. HgI_2 SOLUBILITY AND SOLUBILITY ENHANCEMENT.

Solvent	HgI_2 Solubility (mol solute/mol solvent)	Observed Enhancement (solubility/solubility$_o$)
methyl acetate	0.0010	NO
ethyl acetate	0.0014	NO
n-propyl acetate	0.0022	NO
n-butyl acetate	0.0022	NO
isopentyl acetate	0.0024	1.10
water[24]	3.97×10^{-6}	

NO = no enhancement observed

Table 4. $HgCl_2$ SOLUBILITY AND SOLUBILITY ENHANCEMENT.

Solvent	$HgCl_2$ Solubility (mol solute/mol solvent)	Observed Enhancement (solubility/solubility$_o$)
methyl acetate	0.008	1.34
ethyl acetate	0.085	1.34
n-propyl acetate	0.082	1.54
n-butyl acetate	0.081	1.45
isopentyl acetate	0.065	1.41
methyl formate	0.031	1.51
ethyl formate	0.051	1.32
n-propyl formate	0.049	2.91
n-butyl formate	0.049	2.41
water[24]	0.0046	

diagram and show solubility enhancement of the solute in a "wet" solvent (1.5 to 3 times "dry" solubility). The solute solubilities in "dry" and "wet" solvents are normalized by dividing the ordinate by the dry solubility. Enhancing the solubility implies that on removal of water from the system a slurry of loaded solvent and a pure solid solute will be formed, thus simultaneously drying the solvent and precipitating the solute.

Liquid-Liquid Equilibria

Distribution between a mercuric chloride laden aqueous phase and the organic solvents is shown in Figures 4 and 5 as a function of aqueous concentration. Initial solutions

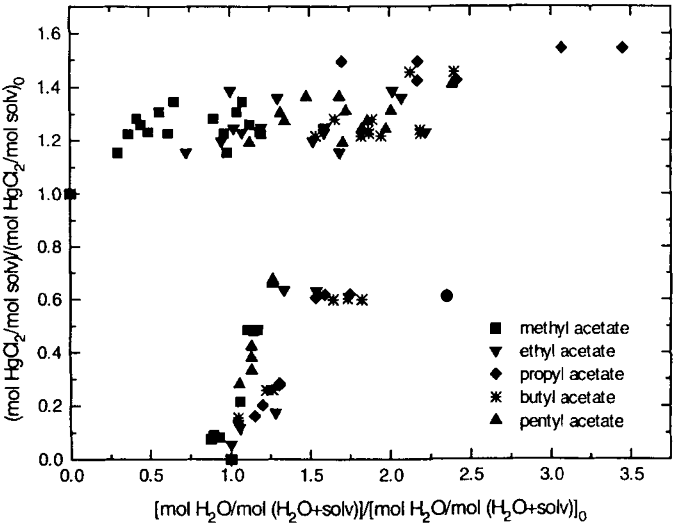


FIGURE 2. $HgCl_2$ enhancement with acetates.

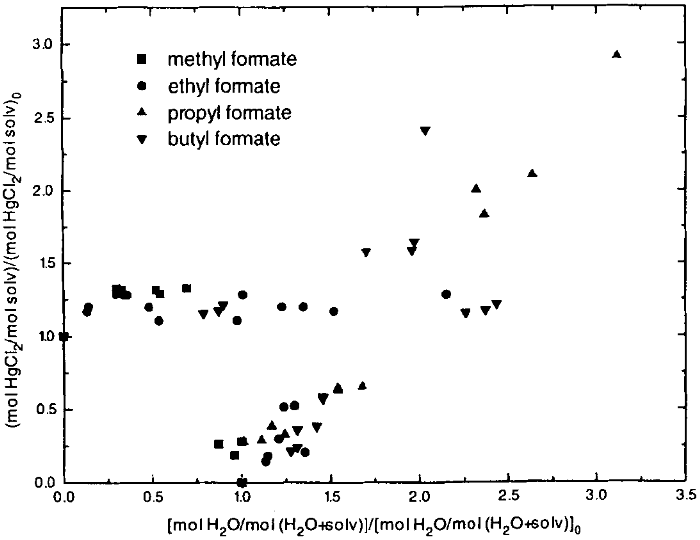


FIGURE 3. $HgCl_2$ enhancement with formates.

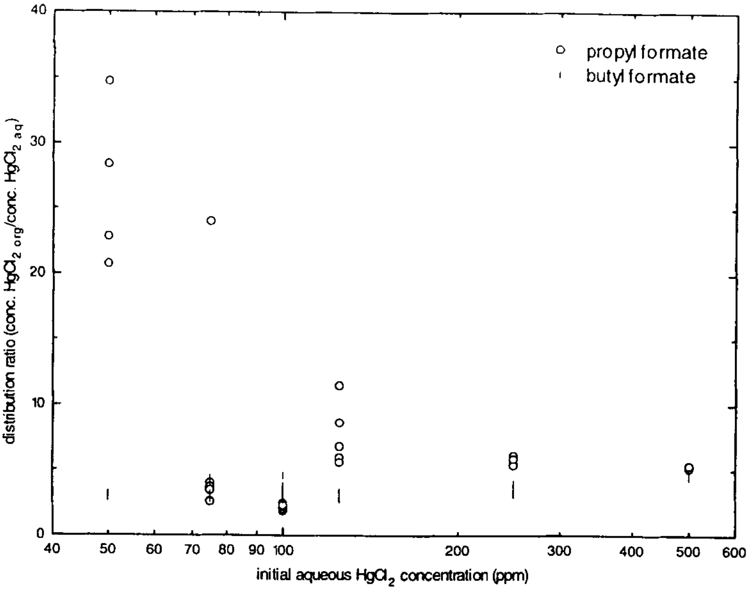


FIGURE 4. Liquid-liquid distribution of $HgCl_2$ in formate-water systems.

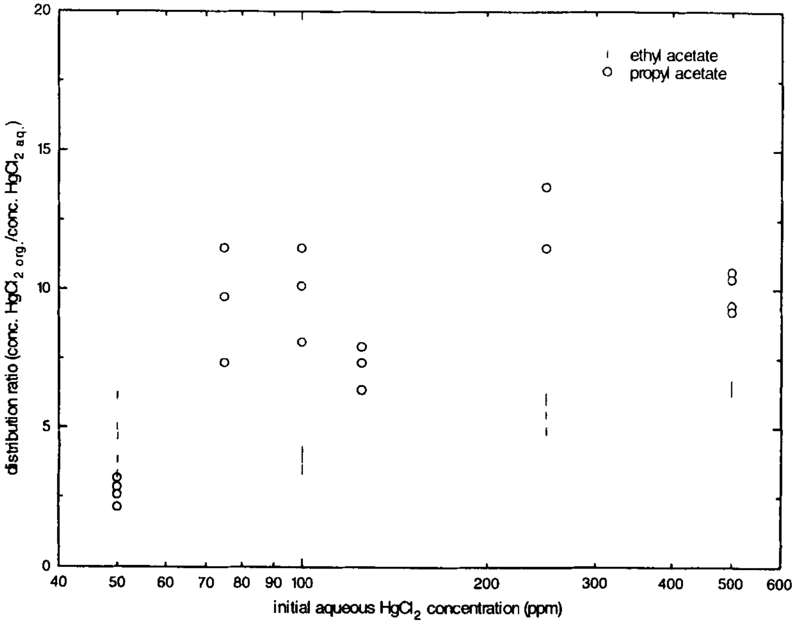


FIGURE 5. Liquid-liquid distribution of $HgCl_2$ in acetate-water systems.

combined 50 - 500 ppm mercuric chloride in water with equal volumes of pure solvent (propyl formate, butyl formate, ethyl acetate, and propyl acetate). The concentration of mercuric chloride in the aqueous phases was measured directly by atomic adsorption spectrophotometry. The organic phase concentrations were determined by backextracting the loaded solvent with a 12% HCl solution and subsequently measuring solute concentrations in the aqueous fraction. Standards for the backextraction were used to predict mercuric chloride concentrations in the original organic phase. Figure 6 shows representative backextraction standards for the ethyl acetate and propyl formate systems and Figure 7 shows the comparison of predicted and actual mercuric chloride in the organic phase. Distribution data show that for ethyl acetate, butyl formate, and propyl formate solvents, the mercuric chloride concentrations in the organic phase are approximately five times the aqueous phase concentrations indicating extremely favorable extraction. The concentration of mercuric chloride in the organic phase with propyl acetate solvent is approximately ten times the aqueous phase concentration. These distributions appear to be constant over the concentration ranges studied. Since mercuric chloride is more soluble in the "wet" than in the "dry" solvent, any of these solvents could be used.

PROCESS DESCRIPTION AND DESIGN

Two solute recovery process designs using ethyl acetate are described. Experimental solubility and distribution data at two representative solute feed concentrations are used (0.05% and 2% mercuric chloride). Table 5 shows the design data, based on a 1000 kg/hr aqueous feed. The Starr-King process[21] consists of: extraction, water removal, and simultaneous solute recovery and solvent regeneration. It was modified to reduce solvent loss in the raffinate by adding a solvent recovery step.

Process feed is contacted with solvent in the extraction step (Figure 1). The solvent to feed ratio and the number of theoretical stages are determined for each feed concentration case using equilibrium and distribution data. The solvent to feed ratio and the number of theoretical stages necessary for solute removal are shown in Table 5. The solute begins to precipitate only after the solvent is fully loaded. The extract is sent to the water removal step, and solvent is recovered from the raffinate in a solvent recovery

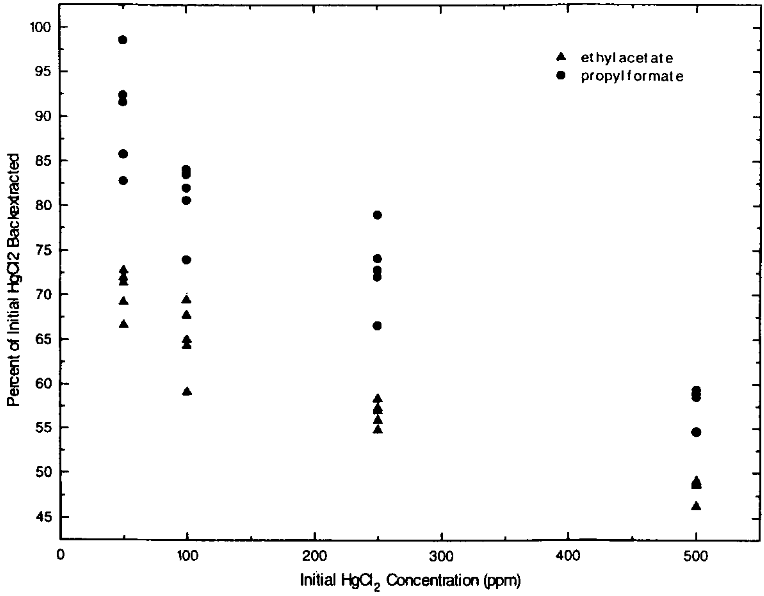


FIGURE 6. Backextraction standards, solvent-mercuric chloride-12% HCl.

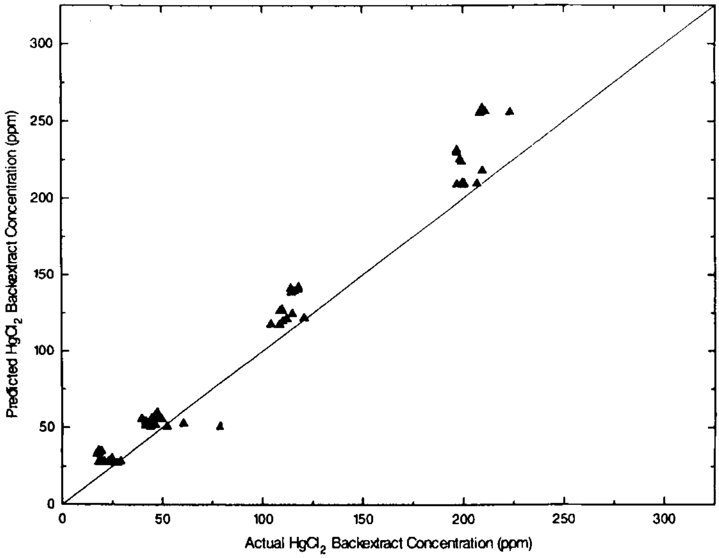


FIGURE 7. Correlation between actual and predicted $HgCl_2$ organic phase concentrations, ethyl acetate-mercuric chloride-12% HCl.

Table 5. DESIGN SUMMARY, 1000 LB/HR FEED RATE BASIS.

$HgCl_2$ (ppm)	Solvent/Feed Ratio	Extraction Staging	Evaporator Duty	Cost*
500	0.25	2	57,998 kJ/hr	[$109/hr]
20,000	0.44	5	64,027 kJ/hr	[$117/hr]

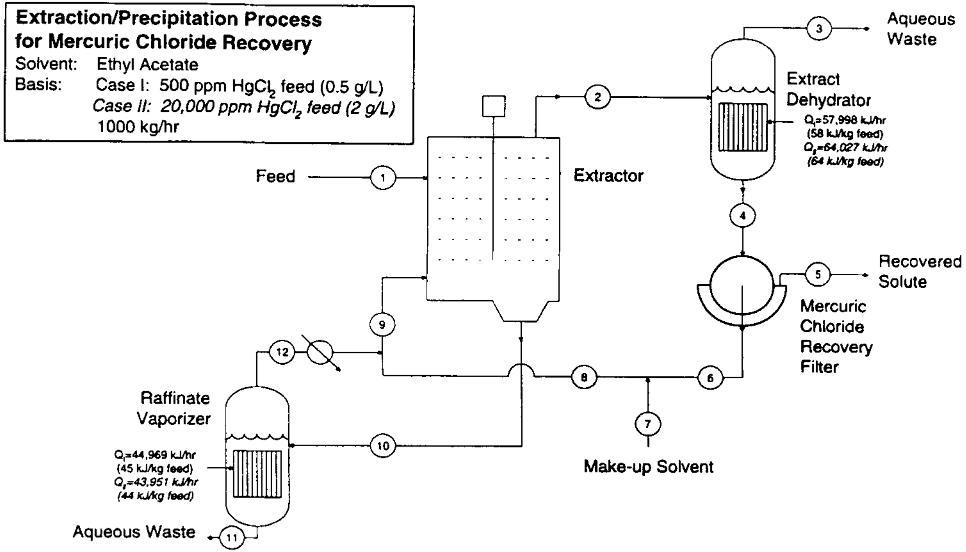
*Total cost based on electrical heating and no solvent recovery (worst case).

step. The volatilities of the raffinate components were estimated using activity coefficient data[25]. The volatility of ethyl acetate was estimated to be approximately 65 times greater than water, implying that recovery from the raffinate will use little energy. The recovered solvent is returned to the solvent stream feeding the extractor. It is conservatively assumed that 1% of the solvent is retained in the raffinate and that 99% is recovered and returned to the extractor.

Water is removed from the extract in the second step (Figure 1). The water also is removed from the extract at a low energy cost since it is a minor fraction of the extract and is preferentially vaporized. Water is preferentially vaporized from the extract because the mercuric chloride solution interacts with ethyl acetate to lower its volatility relative to the water. The relative volatility of the water in the ethyl acetate rich extract is estimated using infinite dilution activity coefficient data[25], and is approximately four. This means that the water will be preferentially evaporated from the extract. It is assumed, conservatively, that only 90% of the water is vaporized in this step. Removing water from the extract forms a slurry containing 0.03% by weight solid mercuric chloride.

The final step recovers the pure solute by a solid-liquid separation (Figure 1). A loaded solvent is formed as water is stripped from the slurry. A conservative estimate of 50% by volume solid cake was used for the design. The remaining cake volume is entrained solvent and water.

As a polishing step, to minimize solvent losses to the environment, a carbon adsorber (or similar method) further reduces the solvent loss in the raffinate, to the solute, and after recovery. Figure 8 shows a process flow diagram for both the 500 ppm and 20,000 ppm cases based on a 1000 kg/hr feed rate. Figure 9 shows the graphical determination



Flow (kg/hr) \ Stream #	1	2	3	4	5	6	7	8	9	10	11	12
Solvent	0.00 *0.00*	112.74 *263.67*	1.12 *2.64*	111.62 *261.02*	0.09 *3.28*	111.53 *257.74*	2.05 *6.77*	113.58 *264.51*	197.46 *346.49*	84.74 *82.83*	0.86 *0.84*	83.88 *81.99*
Water	999.49 *979.98*	24.89 *27.49*	22.42 *24.74*	2.47 *2.76*	0.02 *0.02*	2.45 *2.73*	0.00 *0.00*	2.45 *2.73*	2.45 *2.73*	974.58 *952.49*	974.58 *952.49*	0.00 *0.00*
Mercuric Chloride	0.51 *20.02*	53.00 *112.10*	0.00 *0.00*	53.00 *112.10*	0.51 *20.02*	52.49 *92.09*	0.00 *0.00*	52.49 *92.09*	52.49 *92.09*	0.00 *0.00*	0.00 *0.00*	0.00 *0.00*
Total	1000.00 *1000.00*	190.63 *403.26*	23.54 *27.38*	167.09 *375.88*	0.62 *23.32*	166.47 *352.56*	2.05 *6.77*	168.52 *359.33*	252.40 *441.31*	1059.32 *1035.32*	975.44 *953.33*	83.88 *81.99*

*second line, *italics*, denotes Case II flows

FIGURE 8. Mercuric chloride recovery 500 ppm $HgCl_2$ feed.

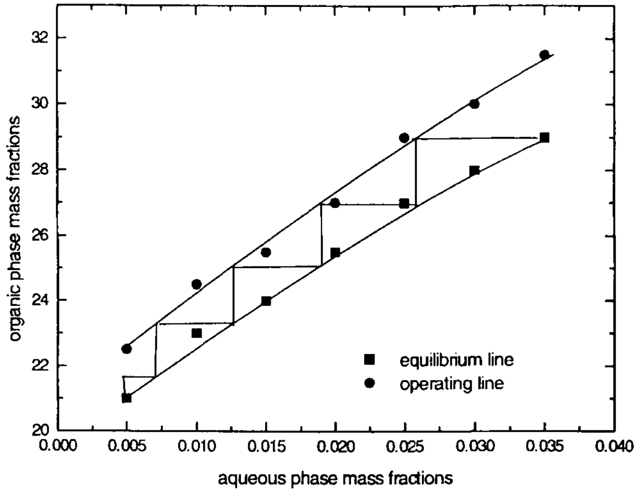


FIGURE 9. Extractor staging requirements, 500 ppm case.

of the extractor staging requirements for the 500 ppm case. Staging requirements for the 20,000 ppm case was similarly determined.

CONCLUSIONS

Experimental data show that enhanced solubilites for mercuric chloride in "wet" organic solvents are a function of the solvent molecular weight for both ester and formate solvents. Enhancements for the mercuric chloride systems studied range from 1.32 to 2.91 moles of mercuric chloride per mole water. Mercuric iodide shows enhanced solubility of 1.10 moles of mercuric iodide per mole water in isopentyl acetate. Zinc(II) chloride shows enhanced solubility of 3.46 moles of zinc chloride per mole water in isopentyl acetate. The system chosen for the preliminary engineering design, mercuric chloride in ethyl acetate, shows an enhanced solubility of 1.34 moles of mercuric chloride per mole water. The enhancement allows the pure solid solute to be recovered as the system's water is evaporated at reasonable costs.

Liquid-liquid equilibria for mercuric chloride in formate and acetate solvents are presented as distribution plots for each solvent class. Ethyl acetate, butyl formate, and propyl formate show distributions, organic mercuric chloride concentration/aqueous mercuric chloride concentration, of approximately five. For mercuric chloride in propyl acetate the D is approximately ten. These distributions are essentially constant over the initial concentration ranges studied.

The extraction-precipitation process based on a 1000 kg/hr feed for recovering pure mercuric chloride from a 20 g/L aqueous solution would cost $2.70 per kilogram mercuric chloride recovered. The organic phase can be loaded almost to the point where the mercuric chloride salt precipitates in a 4 to 5 stage countercurrent extraction column for feed concentrations between 500 and 20,000 ppm mercuric chloride. The solvent to feed ratios for these initial feed concentrations ranged from 0.25 to 0.44. The water could be stripped from the extract with less than 65,000 kJ/hr energy input. The interaction of the mercuric chloride with the ethyl acetate lowered the volatility of the solvent to 25% that of water so that the water can be preferentially stripped from it. When solvent recovery is added to the raffinate stream, the process cost (energy input for water and solvent evaporation and solvent make-up for the 1000 kg/hr, 20,000 ppm case) was calculated to be less than $8 per hour ($0.40 per kg $HgCl_2$ recovered).

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