The Extraction of Mercuric Chloride from Acid Chloride Solutions with Trioctylamine

The equilibrium distribution of mercuric chloride between aqueous sodium chloride solutions and a solution of tri-isooctylamine in xylene has been measured. The dependence on *p*H, amine concentration, mercury level, and temperature has been determined. At low *p*H mercury is extracted quite effectively with a distribution coefficient as high as 2,000. At high *p*H the mercury can be stripped from the organic solution. This extraction system offers the possibility of an effective mercury separation process for chlorine plant brines or chloride-based mercury leach liquors.

A theoretical model of the extraction equilibria is developed to facilitate interpolation of the experimental data.

REINALDO CABAN and
THOMAS W. CHAPMAN

Department of Chemical Engineering
University of Wisconsin
Madison, Wisconsin 53706

SCOPE

For both economic and environmental reasons there is a need for a more effective separation process to extract and to recover mercury from dilute solutions. In mercury-cell chlorine plants in particular, one encounters large volumes of effluent and process streams which must be treated for mercury removal. Direct chemical reduction or ion exchange procedures are not entirely satisfactory because they are either expensive, inefficient, or unable to recover the metal values in a convenient manner.

Because of the success of metal ion solvent extraction processes in nuclear reactor technology and more recently in hydrometallurgical operations where the emphasis is not only on metal separation but also on efficient metal recovery, there are indications that such a process might have an application in mercury recovery technology. The objective of this study with respect to mercury cell chlorine plants is to find a solvent extraction process that is selective for mercury, efficient, and reversible.

It has been known in a qualitative sense that alkyl amines will extract mercuric chloride from acid chloride solutions. In this study the quantitative aspects of the extraction reaction are determined. In particular, the extraction of mercuric chloride from aqueous sodium chloride solutions by tri-isooctylamine in xylene has been studied, and mercury distribution equilibria have been measured over a wide range of mercury concentration. The effects of *p*H, amine concentration, and temperature have been examined as has possible interference from other ions or oxidizing agents.

In addition to direct equilibrium measurements, spectroscopic and vapor pressure measurements have been made to study the structure of the organic amine and metal complex solutions. A theoretical model of the extraction equilibria is proposed which leads to equations for predicting the effects of relevant parameters on the mercury distribution. These should be useful for estimating equilibrium curves in the design range of a specific mercury extraction process.

CONCLUSIONS AND SIGNIFICANCE

It has been found that tri-isooctylamine is an extremely effective extraction agent for mercuric chloride in acidic chloride solutions. For $pH < 2$ and 0.1M amine the distribution coefficient is greater than 100 for aqueous mercury concentrations between 0.01 and 100 μg Hg/ml, reaching a value above 2,000 in the intermediate range. Not only is the extraction efficient but it is also reversible at higher *p*H. At a *p*H greater than 11 the distribution coefficient is found to be as low as 0.1. The effect of elevated temperature is to diminish the distribution coefficients somewhat over the entire *p*H range.

Apparently because of solubility limitations, or possibly because of dimerization, amine concentrations above 0.1M do not enhance the distribution coefficient except at high metal loadings where the capacity is increased.

Studies of the organic solutions indicate that the amine-metal chloride complex exists in a dimeric form, whereas the amine hydrochloride, which is the true extracting agent, is partially dimerized, with the degree of dimerization depending on concentration.

The effect of *p*H on the equilibrium curves can be explained in terms of the formation of an amine hydrochloride salt which, in turn, bonds with mercuric chloride ion pairs. Similarly the effect of chloride concentration, which was not studied experimentally, can be predicted. Because the formation constants for the amine hydrochloride and for mercuric chloride complexes are so high, diminished chloride levels should have little effect on the extraction as long as some excess of chloride is present.

From a practical point of view, not only is the extraction equilibrium favorable for a mercury extraction and recovery process, but the extraction is also very fast with phase disengagement presenting no problem. Also the low aqueous solubilities of amine and xylene indicate minimal reagent losses. Oxidizing agents such as free chlorine have no effect on the system, and other extractable ions, such

---

Correspondence concerning this paper should be addressed to T. W. Chapman.

as iron, interfere with the mercury extraction only to the extent of their relative concentration.

It is suggested then that this extraction system offers interesting possibilities for an effective mercury recovery process. For example, 99.9% of the mercuric ions in a chlorine plant effluent at a level of 10 μg/ml could be extracted at a low *p*H (2 or 3) by an amine solution in five or six equilibrium stages. Proper choice of phase ratios in the extraction and in a subsequent stripping operation at *p*H around 9 to 10 could yield an aqueous mercury solution of concentration as high as 0.5M with a corresponding volume reduction factor of 10^{-4}. This product solution could easily be processed for mercury recovery or recycled. The organic phase is not consumed so that the only reagent requirements in the process are those for *p*H adjustment.

An integrated mercury recycle strategy in a chlorine plant which recaptures mercury from the gaseous and solid effluents requires a process for recovering mercury from subsequent liquid effluents and purge streams. The process proposed here should be suitable for that purpose. Such a mercury concentration process may also find use in a hydrometallurgical process for mercury production.

In our previous paper (Caban and Chapman, 1972) we indicated the need for better mercury recovery procedures for mercury-cell chlorine plants. In particular, one would like to have processes to recover mercury from each of the gaseous, liquid, and solid effluents which, operating in concert, not only accomplish efficient containment of the mercury but also allow economical recycling of the metal without disruption of plant operation. Generally, such processes should avoid introduction of foreign reagents so that additional separation problems are not created.

Satisfactory recovery processes for gaseous and solid effluents do exist, in that sodium hypochlorite solutions, formed by dissolving chlorine in alkaline sodium chloride solutions, are effective in absorbing mercury or mercury salts as soluble mercuric chloride. In principle, the resulting solutions can be recycled to the brine loop, thus returning the mercury to the electrolysis cell. The difficulty with this scheme is that extensive recycling of liquid streams to the brine system requires that some volume of brine must be purged periodically to maintain steady operation. Purging is also required to prevent accumulation of deleterious impurities in the brine. Therefore, one is still faced with the problem of recovering mercury from liquid effluents, particularly mercuric ions from chloride solutions.

Mercuric ions in chloride solutions exist primarily as the anionic tetrachloride complex. Most of the ion exchange processes which have been suggested for mercury recovery take advantage of this fact. The problem with solid anion exchange resins is that the adsorbed mercury is not easily recovered. Also the resins can be blocked by other ions in the solution or attacked by oxidizing agents such as chlorine. To avoid these difficulties yet take advantage of the anionic nature of the mercuric complex in solution, we have investigated the solvent extraction of mercuric chloride by tri-isooctylamine in xylene.

EXTRACTION OF METALS BY LONG CHAIN AMINES

Solvent extraction of metal salts from aqueous solution with long chain amines by ion-pair formation has received increasing attention during the last 10 years. Specificity for extraction, versatility, and high efficiency in many cases have made amines increasingly interesting for the development of new industrial processes; previously, the exploitation of this particular ability of amines was confined to analytical chemistry.

A wide variety of amines have been screened to establish their potentialities as metal extractants from mineral acid solutions (Marcus and Kertes, 1969; Seeley and Crouse, 1966; Seeley and Crouse, 1971; Coleman, 1962). Uranium, cobalt (II) and copper (II) chlorides (Sato, 1966; Sato, 1967; Sato, 1969), exhibiting distribution coefficients with tri-*n*- (and/or iso) octylamine on the order of 100, 100, and 10 respectively, are examples of metals that have been studied in some detail. The list also includes iron (III), indium, and zinc (II), with distribution coefficients on the order of 100, as well as many of the metals encountered in nuclear reactor technology.

The reaction for ion pair extraction by an amine may be expressed formally as

$$MX_{2\,aq} + 2HX_{aq} + 2R_3N_{org} \rightleftarrows MX_4(R_3NH)_{2\,org} \quad (1)$$

In principle, primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) amines behave similarly. Actually, distribution coefficients for a given metal chloride usually increase with isomeric form in the order given, although the order is the inverse for a few metals and for some anions. The solubility of the amine in water decreases markedly as the number of alkyl (R) groups increases and as the length of these alkyl groups increases. Tertiary amines are insoluble in water for most purposes, but they are miscible with nonpolar solvents, and their capacity for metal extraction increases as chain length increases. When the chain gets too long, however, solutions become viscous, the solubility decreases, and steric hindrance effects become noticeable. Therefore, trioctylamine $(C_8H_{17})_3N$, possesses an optimum set of properties which make it best suited for practical processes.

The importance of solvent effects are well known (Marcus and Kertes, 1969), but these effects have not been explained on a sound theoretical basis. Aromatic solvents, for solubility reasons, are usually preferred. Although kerosene is also widely used, modifiers are sometimes required to prevent the formation of a third phase. Among benzene, toluene, and xylene the latter is preferred as one of proved performance in solvent extraction technology (Sato and Adachi, 1969; Roddy and Coleman, 1969).

The extraction of mercury (II) chlorides by secondary and tertiary amines has been reported in the literature (Coleman, 1962; Newman and Klotz, 1961), and distribution coefficients appear to be markedly high although the data are sparse. Complete distribution curves have not been determined previously, particularly with regard to the independent effects of *p*H and chloride level or to the degree of extraction reversibility.

We have investigated the feasibility of mercury extraction from depleted chlorine plant brines with an amine. Such a stream is usually acidic (*p*H = 2.5-3), is still fairly concentrated in NaCl (270 g/l), and contains mercury at a concentration of about 10 to 30 ppm. The extraction system selected on the basis of existing technology for other metals (Brooks and Rosenbaum, 1963; Thornhill et al., 1971; Skobeev et al., 1971) was tri-isooctylamine in mixed xylenes.

EXPERIMENTAL PROCEDURE

Equal volumes of an organic phase and a mercury-containing aqueous phase were contacted vigorously in a separatory funnel until equilibrium was reached.

The organic phase contained tri-isooctylamine (TIOA), 0.1M, dissolved in mixed xylenes (b.p. = 137° to 144°C). The TIOA used was provided by Ashland Chemical Co. as Adogen 381. Adogen 381 is said to contain a minimum of 95% tertiary amines which are isomers of TIOA; the remaining components are mixed amines.

The aqueous phase was prepared to contain 4.63M, or 270 g/l NaCl, which is the typical composition of the depleted brine from the cells in chlor-alkali plants (Macmullin, 1962). Original aqueous solutions were prepared to be of known mercury concentration by adding proper volumes of suitable standard mercuric chloride solutions ($HgCl_2$). These concentrations ranged between 0.1 μg Hg/ml and 10,000 μg Hg/ml and are expressed as μg of Hg^0.

The *p*H was adjusted with NaOH and HCl, as the case required, in order not to introduce foreign ionic species into the system.

Time required to reach equilibrium was on the order of 1 to 2 minutes. A contact time of 4 minutes was generally used.

After contacting, the phases were allowed to separate (which takes only a fraction of a minute), and the concentrations were measured, as was the equilibrium *p*H.

Mercury in the aqueous phase was determined by the so-called "Flameless atomic absorption" method which consists of bringing Hg^{2+} from solution into an inert gaseous stream after reduction to Hg^0 with $SnCl_2$. The air stream is then passed through a cell where optical absorbance at 253.7Å is measured. For this purpose a Coleman MAS-50 Mercury Analyzer was used (Caban and Chapman, 1972).

The difference between the original mercury content and the measured equilibrium concentration in the aqueous phase was assumed to be the mercury in the organic phase. Successive stripping of the organic phase with 0.1M NaOH (in 4.65M NaCl or by itself) allowed quantitative recovery of the mercury. This procedure was used to determine mercury in the organic phase at high *p*H where equilibrium mercury concentrations in the amine are very small. Experimental data for the extraction with 0.1M TIOA at *p*H = 1 and 13 were averaged over 5 to 10 points with a relative deviation of at most 5% in the analysis.

Experiments were conducted at room temperature (72°F ± 2°F, 22°C) and at 70°C, which is the typical temperature of a depleted brine.

The *p*H was measured with a Beckman Electroscan TM 30 and a glass electrode.

Infrared spectra of the organic solutions were taken with a Beckman IR-10 infrared spectrophotometer.

A vapor pressure osmometer, Mechrolab, Inc., Model 301-A, was used for the determination of molecular weights of various species in the organic phase.

MERCURY EXTRACTION EQUILIBRIA

The extraction of $HgCl_2$ by TIOA was verified to be highly effective with maximum extraction being achieved around *p*H = 1. Little or no variation with *p*H was detected between *p*H = 0.5-2.0 where distribution coefficients ($K_D = C_{org}/C_{aq}$) varied from 14 at a C_{org} of 0.1 μg Hg/ml to 65 at C_{org} = 10,000 μg/ml and reached a maximum of 2000 at C_{org} = 500. K_D appears to be above 100 between C_{org} = 0.8 and C_{org} = 2,300 μg/ml at 22°C as shown in Figure 1 for *p*H = 1. Material balance calculations indicate that at maximum loading the amine to metal ratio in the organic phase is 2:1.

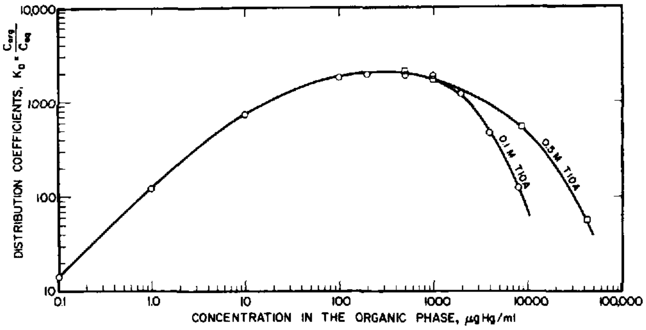


Fig. 1. Mercury distribution coefficient for mercuric chloride in 4.63M NaCl at 22°C and *p*H = 1 as a function of organic phase mercury content. The organic phase is tri-isooctylamine in xylene at 0.1M and 0.5M as indicated.

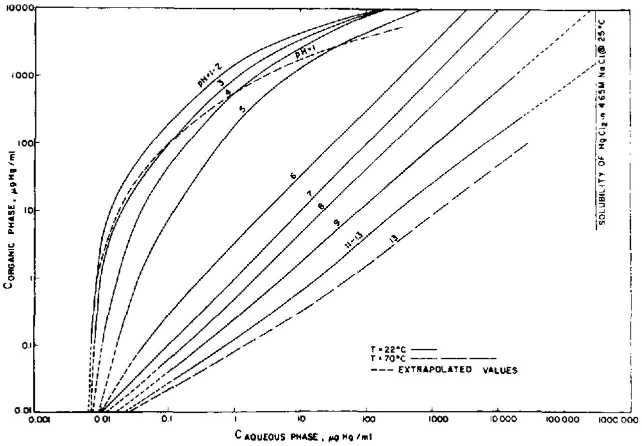


Fig. 2. Mercury equilibrium distribution curves between 0.1M tri-isooctylamine in xylene and 4.63M NaCl in water at various *p*H. Solid lines represent 22°C data. Dashed lines at *p*H = 1 and *p*H = 13 indicate data at 70°C.

On the basic side, *p*H = 13, K_D varied from 0.25 at C_{aq} = 0.1 to 0.023 at C_{aq} = 10,000 μg/ml. (When *p*H = 1, C_{org} describes better the mercury level because most of the mercury is in the organic phase; the opposite is true at high *p*H). Little or no effect of *p*H on the extraction was observed at *p*H between 11 and 13.

On the other hand, the distribution coefficient appeared to be extremely sensitive to equilibrium *p*H at *p*H between 3 and 10. Therefore the data given at intermediate *p*H values are scant and have been interpolated where necessary in the preparation of Figure 2, where the complete equilibrium curves are presented.

Figure 2 presents mercury equilibrium curves for 0.1M TIOA over a wide range of mercury concentrations with *p*H as a parameter. Concentrations are plotted on logarithmic scales which preserve their relative accuracy. Dashed lines indicate data taken at 70°C.

Equilibrium mercury concentration in the aqueous phase increases with temperature at a given total amount of mercury in the system, the increase with respect to values at 22°C being proportionally higher at higher levels of mercury. This can be attributed, in a qualitative sense, to the higher stability of aqueous mercury chloride complexes at higher temperatures, which can otherwise be observed as an increased solubility. From an operational point of view, the reduction with temperature of the distribution coefficient K_D being small at expected working levels (C_{aq} = 0.01 to 1000 μg/ml), presents no major problem; at higher *p*H, the reduction in K_D presents, in any case, an improvement in stripping conditions.

In Figure 3 the distribution coefficient as a function of total amine concentration is presented for an original aqueous phase mercury concentration of 1000 μg/ml ($C_{org} + C_{aq} = 500$ μg/ml) at a *p*H of 1. It is seen that the mercury distribution coefficient levels off at a high value for amine concentrations above 0.1M. This same effect is shown in Figure 1. Except at high aqueous mercury levels, there is no advantage in using an amine concentration higher than 0.1M.

SOLVENT EXTRACTION OF MERCURY FROM BRINES

The equilibrium diagram presented in Figure 2 provides the information needed to characterize the performance of an amine process for extracting mercury from brines in such a way that it can be recovered and recycled.

As an example, a typical depleted brine from mercury-cathode cells in chlor-alkali plants will have a *p*H of about 3, be at 70°C, and contain mercuric chlorides in concentrations of about 10 ppm Hg^0 (with a range from 1 to 50 ppm). Under these conditions the mercury level can be reduced as low as 0.01 μg/ml (10 ppb) by extraction with 0.1M TIOA in xylene at 70°C with the use of a multistage countercurrent contacting system with about six theoretical stages. (Fewer stages will be required if the brine *p*H is lowered to 2.) This will yield a final organic phase concentration of 1,000 μg Hg/ml if an organic to aqueous phase volume ratio, *O/A*, of 0.01 is used. The solubilities of TIOA and TIOA salts in water are almost negligible, and that of xylene in water is also very small. Therefore, the major argument against the use of high *O/A* ratios, namely, loss by aqueous solubility of the organic species, becomes not as compelling as usual. Particularly where the brine is recirculated, for instance to make hypo for gas scrubbing, any such losses will be minimal.

According to Equation (1) enough acid must be added to maintain the brine at a favorable *p*H and to provide the TIOA with the stoichiometric amount required to form the mercury complex. For a brine where $pH \leq 3$ and mercury levels are low these requirements may be insignificant. Since amine volumes are relatively small, the acid required is minimal in any case.

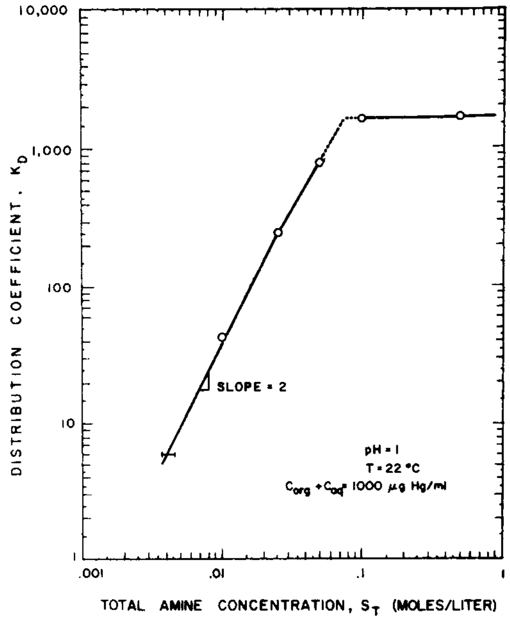


Fig. 3. The effect of amine concentration on the distribution coefficient. *p*H = 1; *T* = 22°C; 4.63M NaCl; $C_{aq} + C_{org} = 500$ μg Hg/ml and equal phase volumes.

In turn the loaded amine can be stripped of nearly all its mercury content with a small volume of brine at an equilibrium *p*H from 9 to 13 (*p*H = 9 seems preferable). Again, enough hydroxide OH^- must be provided to neutralize the HCl in the amine salt and to bring the equilibrium *p*H to the desired value. The resulting aqueous phase can be concentrated in mercury by using a high *O/A* volume ratio. Since the organic phase volume is determined by the previous extraction step, the final aqueous product will have a very small volume. If, in the same example, the organic phase loaded with 1,000 μg Hg/ml is treated with a brine of *p*H = 11 at an *O/A* phase ratio of 100, a resulting aqueous product containing 10^5 μg Hg/ml (0.5M Hg) can be obtained in a volume 10^{-4} as large as the original brine treated.

With the use of proper combinations of phase volume ratios, equilibrium *p*H's and amine molarity, one can concentrate mercury content by a factor as high as 10,000 above that in the original brine. Of course, if the equilibrium aqueous concentration exceeds the solubility of HgO, a precipitate will be obtained. The total mercury concentration at which HgO precipitates at a given *p*H can be obtained from Figure 3 of our previous report (Caban and Chapman, 1972). If it were so desired, NaOH (with no NaCl) could be used in stripping of the amine. However, preliminary experiments show that the distribution coefficients are not as favorable for stripping without excess NaCl. Also the major species recovered would be the HgO precipitate.

The particular choice of operating conditions will be dictated by specific process requirements, convenience, and economics.

The solvent extraction of mercury with amines can also be applied directly to streams where mercury has been oxidized and dissolved with hypochlorite, $O\,Cl^-$, such as those where sodium hypochlorite has been used in the treatment of mercury-containing hydrogen streams and in the treatment of brine sludges in chlor-alkali plants. The use of sodium hypochlorite is also the basis for a new hydrometallurgical process for mercury recovery from low-grade, cinnabar ores, HgS (Parks and Baker, 1969; Parks and Fittinghoff, 1970; Olson and Tveter, 1971). In such systems the $O\,Cl^-$ is oxidized to Cl^- by the half reaction $O\,Cl^- + 2H_2O + 2e^- = Cl^- + 2OH^-$. Hence, after the process of bringing mercury into solution as Hg^{2+} is finished, the system would become similar to the one studied; the chloride ion concentration and the *p*H will be the parameters to be adjusted for optimal operation.

INTERFERENCE FROM OTHER COMPONENTS

In contemplating the application of the amine extraction process to an industrial process stream, we must remember that the data presented are for the highly idealized case where no impurities are present. We should like to know how the extraction will be affected by the presence of certain impurities. For example, a typical brine will show the following analysis (MacMullin, 1962):

Hg	10-50 ppm
Ca	~100 ppm
Mg	1 ppm
Fe	0.3 ppm
Ti	0.1 ppm
Al	~10-50 ppb
Mo	1-10 ppb
Cr	1-10 ppb
V	1-10 ppb
Ni	1-10 ppb
Mn	1-10 ppb

Those with concentrations of 1-10 ppb will present no problem even if they are extracted because their quantity is too low to consume very much amine. Ca, Mg, and Al are not extracted by tertiary amines; this leaves iron (III) as the only extractable species (besides Hg) with a significant concentration. Fe(III) has distribution coefficients with amines on the order of 10^2-10^3 (Marcus and Kertes, 1969; Coleman, 1962).

The effect of iron in NaCl solutions was studied at a mercury level of 1,000 μg/ml, with Fe concentrations from 0 to 2,000 μg/ml. The degree of iron extraction correlates with its wt. % on a Hg + Fe basis as presented in Figure 4, where the mercury distribution coefficient is plotted versus the relative iron level. In particular, the interference with mercury extraction is indicated by Table 1.

Since the iron present in the brine is only 2% of the mercury concentration, it is clear that it will not reduce the mercury extraction significantly. It is reasonable to expect that the reduction in mercury extraction will be close to the amount of extracted iron (although the K_D for Fe is not as high as that for Hg) and that the iron concentration in the organic phase will be about 2% of the mercury concentration.

The effect of dissolved chlorine in the brine was also studied. As mentioned earlier, this is a problem with solid ion exchangers because the resin is destroyed by such a strong oxidizing agent. An experimental extraction was performed from an aqueous phase saturated with Cl_2 (although actual process streams are found to be less than saturated). No significant change in the extraction efficiency was observed.

On the basis of these measurements we conclude that solvent extraction of mercuric chloride from aqueous chloride solutions with tri-isooctylamine (TIOA) offers a convenient and effective way to recover mercury from acid brines (pH 1 to 3). A solvent extraction process using TIOA can be applied to depleted brines in chlor-alkali plants and to other chloride streams where mercury exists in the minute concentrations of 10 to 50 ppm. The mercury content of the treated stream can be lowered to the order of ppb in a few equilibrium extraction stages, and with the proper use of O/A phase ratios a resulting aqueous phase up to 10^4 times more concentrated in mercury than the original can be obtained. Such concentrated solutions can be recycled directly or processed further very easily, from both a practical and an economic point of view.

Moore (1972) has also studied amine extraction of mercury from brines, but he placed emphasis on quaternary amines. These have the advantage of being able to treat alkaline brines. It is rather difficult, however, to recover the mercury from the resulting organic phase. The tertiary amine TIOA can be stripped of virtually all its mercury content by neutralization with strong bases. According to Figure 2, brines of pH 9 or higher have proved to be highly effective stripping agents in this case.

For the rational design of a mercury separation process based on extraction with TIOA, one would like to have complete and accurate equations describing the extraction equilibria. Factors of primary interest are total mercury level, chloride level, pH, amine concentration, and temperature. To make the data in Figures 1 to 3 more useful and to facilitate the interpolation of data, we have sought a theoretical model of the extraction equilibria.

THEORY OF ION PAIR EXTRACTION BY AMINES

The extraction of a metal ion by an amine can be best understood in terms of the formation of an ion pair. The amine forms a salt with a mineral acid H^+X^- of the form $R_3N{:}HX$. When formed by contact of the amine with an aqueous solution of the acid, the resulting amine salt may be hydrated. This salt, which in the case of TOA as R_3N and Cl^- as X^- might be referred to as trioctylamine hydrochloride, can form a bond with a metal salt MX_m (X = halogen, nitrate, sulfate, etc.) when the metal accepts as additional ligands X atoms from amine salt molecules. Generally, in order to have a fairly strong amine salt metal complex, the metal salt should be fairly covalent and should be able to form complexes of the form MX_{m+n}^{-n}. The formation of the metal-amine complex need not take place chronologically in the said two steps; these can take place simultaneously or even by some intricate mechanism. The exact route of such a reaction will be observed only in its kinetics and not in the equilibria.

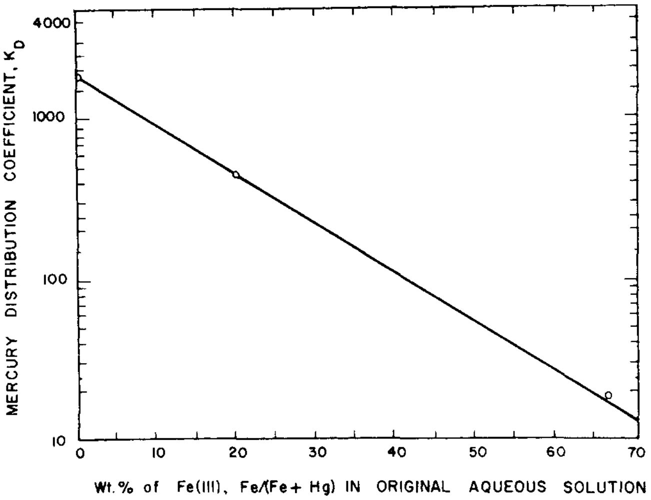


Fig. 4. Effect of iron (III) on the mercury distribution coefficient. $T = 22°C$. $pH = 1$, 0.1M TIOA; 4.63M NaCl; $C_{aq} + C_{org} = 500$ μg Hg/ml and equal phase volumes.

The ionic character of the amine-metal complex in a nonpolar solvent is very minor, and the form written in Equation (1) should not be taken literally but as a convenient formalism. Regardless of the route by which the metal extraction takes place, the equilibrium of this reaction can be represented in terms of a number of simpler equilibria which exist simultaneously among the various species in solution. The problem then is to identify the important molecular species and to estimate individual equilibrium constants.

AMINE SALT FORMATION

Nitrogen with an electronic configuration $1s^2 2s^2 2p^3$ normally engages its $3p$ electrons in bonding while it leaves available for coordination a lone pair of s electrons. Compounds of the type NY_3 show hybridization of sp^3 character which becomes more evident as the Y groups become larger. Thus, tertiary alkylamines are expected to have a nearly tetrahedral configuration.

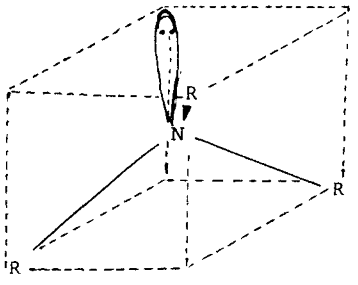


TABLE 1. EFFECT OF IRON LEVEL ON MERCURY EXTRACTION

Wt. % iron, $\left(\frac{\text{Fe}}{\text{Fe} + \text{Hg}}\right)$	Mercury remaining in aqueous phase, μg/ml
0	0.55
20	2.25
66	51.0

Such amines are basic in nature. For example, trioctylamine (TOA) has a pK of 3.0 in benzene. The value in xylene should be quite similar. Acting as a Lewis base, TOA readily donates a pair of electrons. It can thus react with mineral acids of the type

$$H^+X^- \ (X^- = F^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-)$$

in the following manner:

$$R_3N_{org} + H^+_{aq} + X^-_{aq} \rightleftharpoons R_3N{:}HX_{org}; \ K_2 \qquad (2)$$

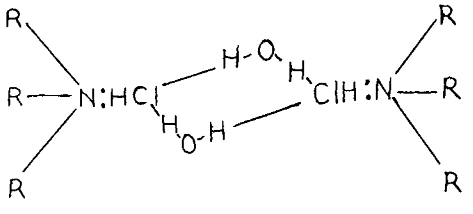
The equilibrium constant for this reaction is quite high, but uncertainties exist regarding the exact value. For example, for TOA in benzene a value of 1.3×10^4 M^{-2} has been reported (Newman and Klotz, 1961) for an organic phase amine concentration between 0.002 and 0.02M, whereas Kakharov and Ochkin (1962) claim $K_2 = 5.5 \times 10^4$ M^{-2} for an amine concentration of 0.227M. Failure to observe consistent values might very well be attributed to the nonideality of the system at high concentrations ($>$ 0.1M).

The literature is full of cases where aggregation of amine salts is presented as the only way to rationalize the peculiar thermodynamic behavior of such salts (Marcus and Kertes, 1969). Even micellar structures containing up to 50 amine salt monomers have been proved to exist. However, for TOA the number of aggregated molecules is not believed to be more than two. Recently Kojima et al. (1969) reported $K_2 = 1.51 \times 10^4$ M^{-2} for TOA hydrochloride in benzene, measured by what seems to be a fairly complete method since they took into account details (such as different types of aggregates) not considered earlier. In particular, using both potentiometric and spectrometric techniques, they established the dimerization reaction

$$2(\text{TOA} - \text{HCl})_{org} \rightleftharpoons (\text{TOA} - \text{HCl})_2; \ K_3 \qquad (3)$$

to be significant at (HCl) $<$ 0.1M with $K_3 = 12.9 \pm 0.5$M^{-1}.

Since it is necessary to postulate the existence of polymers to explain the thermodynamics of amine salt solutions, one might ask, "how do amine polymers form?" It should be recognized at this stage that tri-isooctyl hydrochloride (TIOA-HCl) extracts water into an organic solvent on a 1:1 ratio as shown by Roddy and Coleman (1969). This fact might be very useful to explain the way in which amines dimerize. As the nonpolar alkyl groups interact with the solvent, water bridges are required to join the highly electronegative chlorine atoms. We can thus envision an amine salt dimer of the following structure:



although no direct evidence is available.

METAL COMPLEX FORMATION

We can now consider the formation of amine-metal complexes from amine-acid salts and aqueous metal salts.

No general theory has been established for the selectivity of amines as extractants. We find in most cases that metals that form stable and strong $MX_{m+n}{}^{n-}$ complexes will be extracted by the respective R$_3$N:HX salt by the reaction

$$nR_3N{:}HX_{org} + MX_{m_{aq}} \rightleftharpoons (R_3N{:}HX)_nMX_{m_{org}} \qquad (4)$$

The former property will be a function of size, charge, and softness of both the cation and the anion. Thus cobalt can be separated from nickel because the former forms strong chloride complexes whereas the latter does not, and discriminating extraction with amine hydrochlorides is possible.

In most of the amine extraction cases presented in the literature, the system has been studied at constant original aqueous phase metal concentration in order to observe the effect of the common anion (Cl$^-$, NO$_3^-$, etc.) concentration on the extraction. In only a few cases has a full equilibrium isotherm been generated. This approach is not of interest to us because mercury chloride (Hg Cl$_2$) has a pK $= -13.22$; a change of an order of magnitude in the chloride concentration should not have a very great effect on extraction, as long as the chloride is present in excess. Neither will such incomplete data be of much use for the design of a technical process.

On the other hand, generalized thermodynamic models for characterization of the equilibrium extraction taking into account amine salt and metal complex aggregation as functions of concentration have been proposed. Van Ipenburg (1961), for instance, has developed a theory based on the formation of aggregated amine salts and metal complexes in solution. The application of any such model to obtain a reliable equilibrium expression for metal extraction requires considerable knowledge regarding the molecular species that exist in solution. Therefore, we attempted to obtain information in addition to the extraction equilibria concerning the nature of the mercuric chloride-triisooctylamine hydrochloride solutions in xylene.

INFRARED SPECTROSCOPY

Infrared spectra of amine, amine salt, and metal-amine complex solutions were obtained to study the nature of the extracted species. The most important information conveyed by the individual spectra is that water is present in both the amine salt and the metal complex. This is indicated by strong OH group peaks. Unfortunately, the accuracy is not sufficient to determine whether the ratio of water to amine salt changes when the latter is engaged in metal complexing.

The differential spectra for each of the three pairs of systems were calculated. The predominant metal-chloride species seems to be the tetrachloride with a peak at 440 cm^{-1}.

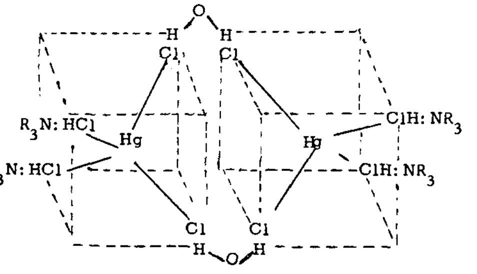
MOLECULAR WEIGHT DETERMINATION

For the determination of the molecular weights of the solute species, vapor pressure osmometry (VPO) was used. The instrument was calibrated with both benzene and anthracene in xylene, and the known molecular weight of TIOA was verified in the absence of chlorides.

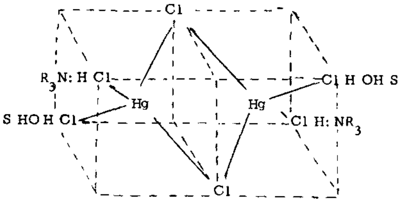
Results show that at infinite dilution the amine salt exists mainly as a monomer. Based on the assumption of a constant activity coefficient for the solvent, the molecular weight (MW) can be determined at other concentrations. In Figure 5 the calculated ratio $MW/MW_{c=0}$ is presented as a function of total amine salt concentration (S_T), or its concentration if it were all monomer. This ratio is the apparent molecular weight of the solute relative to that observed at infinite dilution.

These data indicate that polymerization of the amine salt occurs at finite concentrations. If we assume that only dimers can form, we can calculate from a material balance the amount of dimer that is present. Figure 6 presents the concentrations of salt monomer S and salt dimer S_2 as calculated from Figure 5. Figure 6 shows that at infinite dilution all of the salt is a monomer, whereas as the total amine concentration (S_T) increases the dimer becomes more important. Extrapolation of results to infinite dilution, where the activity coefficients of S and S_2 are constant and can be defined as unity, yields a value for an equilibrium constant for reaction (3) of $K_3 = 7.82$. This value is in good agreement with $K_3 = 12.9$ obtained by Kojima et al. (1969) for TOA·HCl in benzene.

A similar experiment with the metal complex indicates a molecular weight of 2,150 to 2,200 at maximum loading. Combined with a salt to metal ratio of 2:1 determined for such conditions, this value corresponds to a complex dimer $M_2S_4 \cdot 4H_2O$ with $MW = 2{,}170$ in which all salts preserve their single water molecule. IR data are not sufficiently sensitive to indicate whether the metal complex has two or four water molecules, but the lack of a differential peak between the spectra for the salt and metal complex hints that all four water molecules are retained. A series of arguments may be made for and against the latter statement; this issue has great relevance to the possible stereochemistry of the complex species. First, there being four chlorines coordinated to each mercury, only two of them can be engaged in monomer-monomer bonds because of the tetrahedral configuration of Hg^{2+} and because the other two chlorines are linked to the bulky trioctylamine molecules. Second, if the two monomers are linked via water bridges, there is the possibility of using either two or four water molecules. If the latter is the case, one may think that the bond should not be as strong as it appears to be (that is, no metal complex monomer exists) since the chlorines coordinated to mercury should not be sufficiently electronegative to hydrogen-bond with two water molecules. On the other hand, if only two water molecules are bridging the two monomers, the other two can be associated with chlorines in some other fashion, as long as there is no steric hindrance, and they are shielded from the nonpolar solvent. For example, a possible structure is



Another possible complex structure is



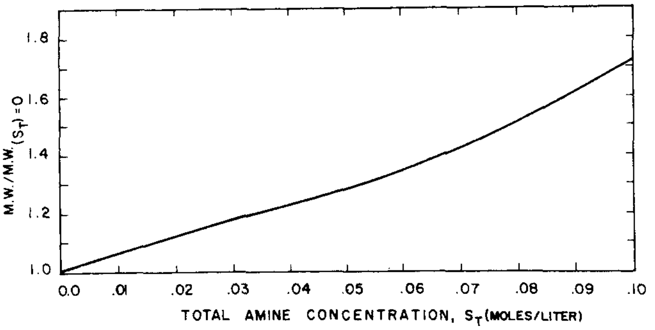


Fig. 5. Relative apparent molecular weight of triisooctylamine hydrochloride vs. total amine hydrochloride concentration in xylene as determined by vapor pressure osmometry.

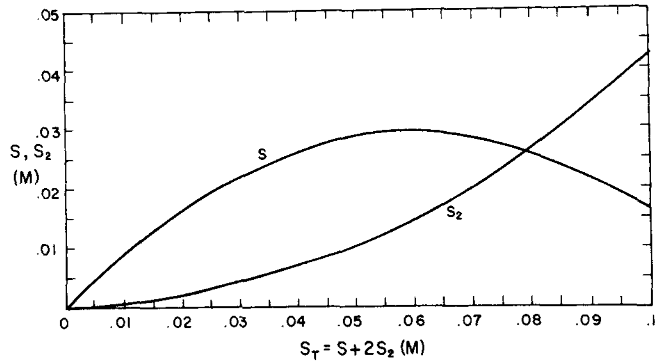


Fig. 6. Concentrations of amine hydrochloride monomer and dimer vs. analytical amine salt concentration, calculated from Figure 5.

Such a structure as the latter will imply, however, that only two of the amine salts are strongly bonded to mercury leaving open the possibility that at a deficit of amine salt, a salt to metal ratio of 1:1 could be obtained, contrary to the observed 2:1 ratio. Whichever may be the case, the definite evidence at this time indicates that the mercury is coordinated with four chlorines and that the metal complex monomer-monomer bond must be very strong since we do not have any evidence of the existence of the metal complex monomer in any detectable quantity. Even at infinite dilution, VPO data for the metal complexes indicate that the complex monomer does not exist.

INTERPRETATION OF THE MERCURY EXTRACTION EQUILIBRIA DATA

Any attempt to fit a simple model to the equilibrium data presented in Figures 1 to 3 quickly reveals that the mercury extraction reaction is more complicated than one might expect. If the reaction occurred as it is written in (1), the equilibrium curves in Figure 2 should have a slope of unity at low loadings, and there should be a more regular variation with pH.

Figures 1 and 3 also indicate strange behavior with respect to amine concentration. At low amine levels, the reaction appears to be second order in amine as one might expect. At amine levels above 0.1M, however, the degree of extraction is not enhanced further, except at high loadings. This behavior, which is described as a constant amine activity, has been reported for a number of cases (Marcus and Kertes, 1969; Coleman, 1962; Sato, 1966; Sato, 1967; Brooks and Rosenbaum, 1963). At the present time no definite explanation of this phenomenon is available. Some have attributed it to the formation of micellar amine salt structures, but this seems unlikely in our case. It does seem probable, however, that some solubility limitation is involved. Anhydrous trioctylamines are known to be completely miscible with aromatic solvents. When the hydrated chloride salt forms, its solubility may very well be limited. In our case no third phase was detected during any of the experiments. When a special effort was made to nucleate a third phase from the salt solution, it was possible to form a fine white precipitate, but the amount was so small that analysis was not possible. Thus, it appears that third phase formation may be occurring in these systems even though it is not readily detected by casual observation.

Another strange characteristic of the mercury equilibrium curves in Figure 2 is that all curves approach a low asymptotic aqueous mercury level of 0.00635 μg/ml. There is no theoretical basis for such behavior, but it is not difficult to rationalize. We might speculate that it results from the aqueous solubility of some organic mercury complex. At such a low level of mercury the issue is not of much practical importance, and detailed calculations are not justified. We note, however, that if the aqueous mercury concentration is corrected by subtracting the asymptotic value 0.00635 μg/ml, one obtains a corrected equilibrium curve which has a more normal appearance. In particular, at $pH = 1$, this corrected equilibrium curve exhibits a first-order dependence of $(Hg)_{org}$ on $(Hg)_{aq}$ over a wide range of mercury level. At very low levels of mercury, however, below $(Hg)_{aq} = 0.01$ μg/ml, the dependence appears to become second order. This behavior is shown by the corrected data points in Figure 7.

Whether such an ad hoc correction of the equilibrium curves is legitimate is not clear. Because the mercury levels in this range are so low, more complete chemical analysis is not feasible. We are, therefore, content to admit uncertainties in this very dilute range and to accept the correction as an empirical parameter.*

The asymptotic behavior of the equilibrium curve at low pH is to be expected as all the amine is converted to salt, according to Equation (2). The behavior at high pH is more surprising. One might expect the distribution coefficient to decrease with increasing pH rather than reaching an asymptotic form at $pH \geqq 11$. The finite organic phase solubility of mercury at these higher pHs as shown in Figure 2 probably reflects the solubility of some hydroxide compound rather than the chloride. Because this solubility and the corresponding distribution coefficient are rather low, this aspect of the system is not of great practical importance. For the purposes of process design we have focussed attention on the equilibria in acidic solutions.

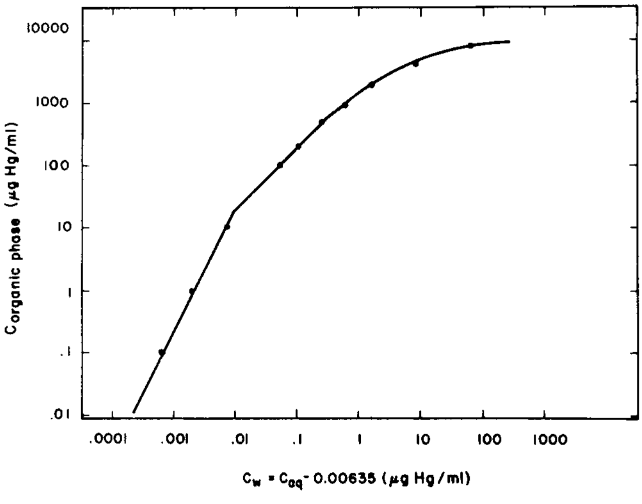


Fig. 7. Corrected equilibrium data for $pH = 1$, $T = 22°C$, 4.43M NaCl; 0.1M TIOA. Abscissa is $(C_{aq} - 0.00635)$ in μg Hg/ml. Line for $C_{org} < 10 \mu$g Hg/ml is plot of Equation (14) with $K_5K_6 = 1.78 \times 10^{21} M^{-5}$. Line for $C_{org} > 10$ μg Hg/ml is plot of Equation (15) with $K_6(C_1)^* = 2.84 \times 10^8 M^{-5}$.

A THEORETICAL MODEL FOR THE EXTRACTION EQUILIBRIA

A theoretical model for mercury extraction from acidic chloride solutions must account for the following phenomena:

1. The reaction is of second order with respect to the corrected metal concentration in the aqueous phase at very low concentrations.
2. Dependence on aqueous mercury concentration changes rather abruptly to first order at higher mercury levels.
3. The mercury complex in the organic phase is a dimer.
4. At the limiting amine-loading condition the ratio of metal to total amine salt is 1:2.
5. At low amine salt concentrations the reaction is of second order with respect to the amine salt.
6. There is an amine salt concentration around 0.1M above which the distribution coefficient is independent of salt concentration.
7. The organic phase mercury appears to be coordinated by four chloride ions.
8. There are water molecules involved in both the amine salt and the metal complex.
9. The amine salt is partially dimerized at finite concentrations.

One scheme for explaining the rather complicated behavior of this system is the following pair of reactions which may occur simultaneously with the salt formation reaction (2) and the salt dimerization reaction (3):

$$M + 2S \rightleftharpoons C_1 \,;\, K_5 \tag{5}$$

$$C_1 + 2S + M \rightleftharpoons C_2 \,;\, K_6 \tag{6}$$

where M is aqueous mercuric chloride, S is amine salt monomer, and C_1 and C_2 are two different mercury complexes. In addition, we propose that C_1 is a mercury complex monomer of such low solubility $(C_1)^*$ that it escapes detection in vapor pressure measurements and C_2 is the dimer. Also, the values of the equilibrium constants in this case must be such that a significant amount of C_1 never precipitates.

Additional equilibria that must be considered under various conditions are the formation of the $HgCl_2$ (reactant M) and HCl ion pairs in the aqueous solution and possibly the precipitation of amine salt at its apparent solubility of 0.1M. When the pH is less than two and the amine concentration is less than 0.1M, essentially all of the amine is converted to salt, and the relevant equilibrium expressions become

$$\frac{[C_1]}{[S]^2\,[M]} = K_5 \tag{7}$$

$$\frac{[C_2]}{[S]^2\,[M]\,[C_1]} = K_6 \tag{8}$$

and

$$\frac{[S_2]}{[S]^2} = K_3 \tag{9}$$

When there is enough mercury to saturate the solution with C_1, there is the additional constraint

$$[C_1] = [C_1]^* \tag{10}$$

---

* Subsequent measurements have shown that, even in the absence of mercury, acidic brines extract some amine, and this amine gives a false reading in the mercury analysis on the order of 0.006 μg Hg/ml. A correction in the measured aqueous mercury level is therefore appropriate.

For the low mercury levels where $(C_1) < (C_1)^*$, Equations (7), (8), and (9) yield

$$[C_2] = \frac{K_5 K_6}{K_3^2} [S_2]^2 [M]^2 \qquad (11)$$

To relate this equation to the experimental data, we make the approximation that activity coefficients are unity so that activities [ ] may be replaced by concentrations ( ). Then mercury concentration in the organic phase can be written

$$\begin{aligned}(Hg)_{org} &= (C_1) + 2(C_2) \\ &= \left\{ 1 + 2\frac{K_6}{K_3}(S_2)(M) \right\} \frac{K_5}{K_3}(S_2)(M) \qquad (12)\end{aligned}$$

For the aqueous phase (M), the concentration of $HgCl_2$ depends on total ionic mercury content, chloride level, and pH (Caban and Chapman, 1972; Butler, 1964; Ciavatta and Grimaldi, 1968; Ciavatta, 1968; Deacon, 1963; Eliezer, 1965). For acidic 4.63M NaCl at 25°C,

$$(M) = \frac{(Hg)_{aq}}{1520} \qquad (13)$$

Because the corrected experimental data at low concentrations show $(Hg)_{org} \propto (Hg)^2{}_{aq}$, Equation (12) indicates that (C_1) is always small compared to (C_2). The distribution curve in this range is thus represented by

$$(Hg)_{org} \doteq \left[\frac{K_6 K_5}{760\, K_3^2} \right] (S_2)^2\ (Hg)^2{}_{aq,c},\ (C_1) < (C_1)^* \qquad (14)$$

In this equation, $(Hg)_{aq,c}$ is the analytical mercury content in the aqueous phase corrected for the anomalous asymptotic value by subtraction of 0.00635 μg/ml.

At higher levels of mercury $[C_1]$ becomes a constant $[C_1]^*$, and Equations (7), (8), and (9) yield

$$(Hg)_{org} \doteq 2(C_2) = \left[\frac{K_6 (C_1)^*}{760} \right] (S)^2\ (Hg)_{aq,c},\quad (C_1) \geqq (C_1)^* \qquad (15)$$

Equations (14) and (15) describe the low pH equilibrium data shown in Figures 1, 2, and 3. More specifically, they predict the change in slope of the corrected equilibrium curve in Figure 7. The values of the coefficients may be obtained from the equilibrium data. From the maximum distribution coefficient in Figure 1, 2010, we obtain $[(C_1)^* K_6] = 2.84 \times 10^8\ M^{-5}$. From the corrected data at low mercury levels where the slope is two on Figure 7 we obtain $[K_5 K_6] = 1.78 \times 10^{21}\ M^{-5}$. The value of K_3 can be estimated from Figure 6. In addition, we can calculate $\frac{[C_1]^*}{K_5} = 1.6 \times 10^{-13}\ M^3$. This value allows the calculation of the aqueous mercury level at which $[C_1]$ reaches $[C_1]^*$ by combination of Equation (7) and the mercuric chloride formation equilibrium [for example, Equation (13)].

As the organic solution approaches full loading, the amine salt concentration is not constant but is diminished by mercury complex formation. A material balance on amine salt yields

$$S_T = (S) + 2(S_2) + 2(Hg)_{org} \qquad (16)$$

At higher pH, where salt formation is not complete, the equilibrium of reaction (2) must also be considered in the amine balance. In either case an appropriate substitution for (S) in Equation (15) should be made to express the equilibrium in terms of total amine and the mercury level. The formation of dimer as indicated by Figure 6 must also be used.

For the case of $pH = 1$, $T = 22°C$, and $(TIOA) = 0.1M$, the corrected equilibrium data have been compared with Equations (14) and (15) in Figure 7. The data below $(Hg)_{org} = 500$ μg/ml fall quite nicely on the straight lines predicted by the equations, the precise agreement in this region resulting from the adjustment of one constant coefficient for each equation. What is gratifying in this comparison is the agreement above $(Hg)_{org} = 500$ μg/ml where Equation (16) and Figure 6 have been used to compute (S) in Equation (15). It appears that these equations provide a reasonably correct representation of the mercury extraction equilibria at 25°C. Equation (15) in particular can be used to estimate the effect of amine concentration, pH and mercury level on the mercury extraction equilibrium in the region of practical interest.

ACKNOWLEDGMENT

This work was supported by grants from the Department of Natural Resources of the State of Wisconsin, The Research Committee of the Graduate School, and the Institute for Environmental Studies of the University of Wisconsin, Madison.

NOTATION

(C_1) = concentration of metal complex monomer, g-moles/l
$(C_1)^*$ = solubility of metal complex monomer, g-moles/l
(C_2) = concentration of metal complex dimer, g-moles/l
C_{aq} = concentration of mercury in aqueous phase, μg/ml
C_{org} = concentration of mercury in organic phase, μg/ml
$(Hg)_{aq}$ = concentration of mercury in aqueous phase, g-moles/l
$(Hg)_{org}$ = concentration of mercury in organic phase, g-moles/l
K_D = equilibrium distribution coefficient = C_{org}/C_{aq} = $(Hg)_{aq}/(Hg)_{aq}$
K_i = equilibrium constant for Reaction (i), molar units
(M) = concentration of $HgCl_2$ in aqueous phase, g-moles/l
(S) = concentration of amine salt monomer, g-moles/l
(S_2) = concentration of amine salt dimer, g-moles/l
S_T = total analytical amine salt concentration, g-moles/l

LITERATURE CITED

Books, P. T., and J. B. Rosenbaum, *Separation and Recovery of Cobalt and Nickel by Solvent Extraction and Electrorefining*, Bureau of Mines Report No. 6159 (1963).

Butler, J. N., Ionic Equilibria—A Mathematical Approach, pp. 297-303, Addison-Wesley, Reading, Mass. (1964).

Caban, R., and T. W. Chapman, "Losses of Mercury from Chlorine Plants—A Review of a Pollution Problem," *AIChE Journal*, **18**, 000 (1972).

Ciavatta, L., and M. Grimaldi, "Equilibrium Constants of Mercury (II) Chloride Complexes," *J. Inorg. Nucl. Chem.*, **30**, 197 (1968).

———, "Hydrolysis of Mercury (II) Chloride, $HgCl_2$," *ibid.*, **30**, 563 (1968).

Coleman, C. F., *Amines as Extractants—Survey of the Descriptive and Fundamental Extraction Chemistry*, Oak Ridge Nat. Lab. Report No. 3516, Tenn. (1962).

Deacon, G. B., "Chemistry of Halomercurate (II) Complexes," *Rev. Pure Appl. Chem.*, **13**, 189 (1963).

Eliezer, E., "Solubility and Structure of Mercuric Chlorides," *J. Chem. Phys.*, **42**, 3625 (1965).

Kojima, Takashi, H. Fukutomi, and H. Kakihana, "Extraction of Hydrochloric Acid by Tri-n-octylamine in Benzene," *Bull. Chem. Soc. Japan*, **42**, 875 (1969).

MacMullin, R. B., "Electrolysis of Brines in Mercury Cells" in *Chlorine, Its Manufacture, Properties, and Uses.* Am. Chem. Soc. Mono. Ser. No. 154 (1962).

Marcus, V., and A. S. Kertes, Ion Exchange and Solvent Extraction of Metal Chelates, Ch. 10., Interscience, New York (1969).

Moore, Fletcher L., "Solvent Extraction of Mercury from Brine Solutions with High Molecular Weight Amines," *Environ. Sci. Technol.*, **6**, 525 (1972).

Newman, L., and P. Klotz, "The Interaction of Tri-n-octylamine with Thenoyltrifluoroacetone and with Hydrochloric Acid," *J. Phys. Chem.*, **65**, 796 (1951).

Olson, Robert S., and Elmer C. Tveter, "Mercury Ore Leaching Process," U.S. Pat. 3,627,482 (1971).

Parks, G. A., and R. E. Baker, "Mercury Process," U.S. Pat. 3,476,552 (1969).

Parks, G. A., and N. A. Fittinghoff, "Mercury Extraction Now Possible via Hypochlorite Leaching," *Eng. Mining J.*, **107** (1970).

Roddy, J. W., and C. F. Coleman, "The Extraction of Water by Tri-n-octylamine and Several of Its Salts in Benzene and Phenylciclohexane," *J. Inorg. Nucl. Chem.*, **31**, 3599 (1969).

Sato, Taichi, "The Extraction of Uranium (VI) from Hydrochloric Acid Solutions by Tri-n-Octylamine" *ibid.*, **28**, 1461 (1966).

———, "The Extraction of Cobalt (II) from Hydrochloric Acid Solution by Tri-n-Octylamine," *ibid.*, **29**, 547 (1967).

———, and K. Adachi, "The Complex Formed in the Cu II—HCl—TOA Extraction System," *ibid.*, 31, 1395 (1969).

Seeley, F. G., and D. J. Crouse, "Extraction of Metals from Chloride Solutions with Amines," *J. Chem. Eng. Data*, **11**, 424 (1966).

———, "Extraction of Metals from Nitrate and Sulfate Solutions with Amines," *ibid.*, **16**, 393 (1971).

Skobeev, I. K., A. S. Sinakevich, and N. V. Bardik, "Extraction of Molybdenum by Technical TIOA from Solutions of Soda Leaching." *Ekstr. Sorbtsiya Met. Modibdena,* Vol' frama Reniya, 42-7, (1971). From Chem. Abstr. 76:36312M.

Thornhill, P. G., E. Wigstol, and G. VanWeert, "The Falconbridge Matte Leach Process," *J. Metals*, **23**, 13 (1971).

Van Ipenburg, K., "Liquid-Liquid Extraction of Metal Salts from Acidic Solutions Using Amine Salts," *Rec. Trav. Chim.*, **80**, 269 (1961).

Zakharov-Nartisissov, O. I., and A. N. Ochkin, "Extraction of Nitric Acid with Tri heptylamine," *Russ. J. Inorg. Chem.*, **6**, 1936 (1961).

———, "The Extraction of Certain Strong Monobasic acids with Trioctylamine," *ibid.*, **7**, 665 (1962).

Calculation of Multicomponent Liquid-Liquid Equilibrium with Renon's and Black's Activity Equations

The combination of optimization theory and thermodynamics was used to develop a fast, reliable computerized procedure for predicting or representing multicomponent liquid-liquid phase equilibrium. Both the Renon and Black activity coefficient equations were compared with experimental data using the procedure. Experimental data for three quarternary systems from the literature were examined. Prediction of ternary data from binary data is not very reliable, although ternary data can nearly always be represented by adjustment of the predicted binary constants. Quarternary data can be predicted from accurate ternary representations of similar species provided the additional compound is from the same family group. The Renon equation is recommended rather than the Black equation.

CHARLES G. GUFFEY and
ALBERT H. WEHE

Department of Chemical Engineering
Louisiana State University
Baton Rouge, Louisiana

SCOPE

In the design of extraction equipment, it is necessary to represent graphically or analytically experimental liquid-liquid phase equilibrium data so that the data can be interpolated or extrapolated. In the past, this has been done primarily with algebraic, graphical correlations which lent themselves readily to graphical design procedures. Twenty-six calculation methods have been reviewed by Guffey (1971). These procedures can be time consuming and involve approximations.

Previous procedures can be divided into those intended for the correlation of ternary and quaternary experimental data and those for prediction of quaternary from ternary or

---

Correspondence concerning this paper should be addressed to A. H. Wehe, Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803. C. G. Guffey is at Humble Oil and Refining Company, Baytown, Texas 77520.