Solvent Extraction of Metal Ions and Surface Active Agents from Saturated Sodium Chloride Brine

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Metal ions and surface active agents can be extracted from saturated sodium chloride brine using isopropyl alcohol as the solvent. Detergents are extracted completely in concentrations of 2×10^{-3} M. Above this concentration, precipitation occurs. Most metal ions are only slightly extracted, having distribution ratios smaller than 1. However, gold(III), titanium(IV), and vanadium(IV) are well extracted, having distribution ratios of 125, 6.8, and 10.6, respectively. Iron(III), gallium(III), indium(III), tin(II), and vanadium(V) also have distribution ratios greater than 2 but smaller than 4.

SOME SEMIPOLAR LIQUIDS which are normally miscible with water form a two-phase mixture when added to strong salt solutions (*19*). An example is the dioxane-ammonium sulfate system. Comar (2) outlines a number of systems used to extract metal ions, drugs, and amino acids from strong salt solutions. There are undoubtedly important applications of these systems in industrial water conversion projects, particularly in the analysis and recovery of minerals and organic residues from brines (*3, 4*).

Methods for extracting materials from brines, including sea water, using solvent extraction are relatively few (*18*). Boron (*10*) and bromides (*1*) have been studied using solvents which are normally miscible with water. Fresh water has been extracted from saline water using low molecular weight amines, which are normally miscible with water at low temperatures but separate into a water-rich, salt-free phase at higher temperatures (*3, 4*). Recently Deshmukh and Rao (*5, 6*) found that cobalt(II) and nickel(II) are preferentially extracted from greater than $3M$ sodium formate solutions using pyridine, an amine normally miscible with water. In this work, the authors have explored the extraction of metal ions and surface active agents from brines using an approach based on normally water-miscible solvents as extracting phases. Isopropyl alcohol-sodium chloride brine systems are best for extracting detergents, gold(III), titanium(IV), and vanadium(IV).

EXPERIMENTAL PROCEDURE

Solutions of metal salts and detergents were prepared by dissolving the chloride or nitrate in sodium chloride solutions, saturated at 24° C. The metal ion solutions were prepared by weighing the salts and diluting to $10^{-3}M$. The exact concentration of each metal ion in the solution was measured using polarography. Surface active agents were sodium lauryl sulfate, recrystallized three times from ethyl alcohol and dried; Hyamine-1622 (trade-name, Rohm & Haas Chemical Co., Philadelphia, Pa.) and Benax-2A1 (trade-name, Dow Chemical Co., Midland, Mich.). Hyamine-1622 [diisobutyl phenoxyethoxyethyl dimethylbenzylammonium chloride, monohydrate (m.w. 466.1)] is a representative quaternary ammonium detergent. Benax-2A1 (40% aqueous sodium salt of dodecylphenoxybenzene disulfonate) is an aromatic sulfonic acid type detergent. The molecular weight was in doubt because the product was a mixture of mono- and dialkylated product. This product was measured by direct dilution rather than by preparation of a stock solution. Solutions measuring 2×10^{-3} M in surface active agent concentration were used in this work, except in the case of Benax-2A1, which was used at a concentration of 2 parts per thousand of the commercial product solution.

The solution of each compound in saturated sodium chloride brine was extracted with an equal volume of isopropyl alcohol. The metal ion content of the solution was known by prior polarographic analysis of the stock solutions. After the extraction, the volume of aqueous and organic phases was measured, and the metal content of the aqueous phase measured polarographically (*16*). The distribution ratio was then calculated using polarographic diffusion current data according to the equation:

$$D = \frac{i_{d,\,in.} - i_{d,\,f.}}{i_{d,\,f.} - i_{d,\,r.}} \times \frac{V_w}{V_o}$$

where $i_{d,\,in.}$ is the initial diffusion current of the metal ion in solution before the extraction, $i_{d,\,f.}$ is the diffusion current after the extraction, $i_{d,\,r.}$ is the residual current of the aqueous phase, V_w is the volume of the aqueous phase, and V_o is the volume of the organic isopropyl alcohol phase. Where dilution of the solution was necessary, corrections were made in the diffusion current to make certain that all measurements were on the same reference basis.

The surface active agents which contained benzene functions were analyzed using ultraviolet spectrophotometry. The Benax-2A1 absorption peak was located at 280 mμ (2×10^{-4} dilution). The molar absorptivity of the compound could not be estimated because the commercial product has an indefinite composition. The Hyamine-1622 was measured at 276 mμ (molar absorptivity = 1772). The compounds were measured in pure isopropyl alcohol solvent. The distribution ratios were measured using isopropyl alcohol pre-equilibrated with saturated sodium chloride. It was established that the absorption maximum did not shift with a solution composition change, and knowledge of the molar absorptivity was not necessary for calculation of the distribution ratio.

Sodium lauryl sulfate was analyzed spectrophotometrically using the method of Hedrick and Berger (*14*). In higher concentrations, both Hyamine-1622 and sodium lauryl sulfate were analyzed by titration with the other surface active agent according to the method of Hwa (*15*).

Magnesium could not be determined polarographically, and was determined by titration with disodium ethylene(dinitrilo)tetraacetate at pH 10, using Eriochrome Black T as the metallochromic indicator. The distribution

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ratio of gold(III) in all systems was measured using spectrophotometric analysis at 310 mμ. To establish a numerical value for the distribution ratio, the molar absorptivity of the gold(III) chloride complex was measured in saturated sodium chloride solution. The spectrum of the complex in solution was the same whether or not isopropyl alcohol was present. The distribution ratio of the gold(III) chloride complex was measured by adding 50.0 mg. of sodium tetrachloroaurate(III) to 20.0 ml. of saturated sodium chloride solution. The mixture was then equilibrated with an equal volume of isopropyl alcohol. The absorbance of the gold-containing sodium chloride solution was measured at 310 mμ and the weight of sodium tetrachloroaurate(III) calculated from spectrophotometric measurements. The distribution ratio was then calculated after applying a volume correction. The numerical results obtained for gold represent an average of four determinations, with a standard deviation of 9 distribution ratio units. The rate of extraction of gold appears to be very rapid, based on qualitative observations.

The analytical procedure used for mercury(II) was performed by adding an equal volume of isopropyl alcohol to the salt water phase, then adding a small amount of Thiomichler's ketone as a metallochromic indicator. The solution was then titrated using monothioglycerol. The color change for the indicator is purple to yellow in this system. For analysis of the isopropyl alcohol layer, an equal volume of water is added before the indicator. This method follows from work done by Fritz and Palmer (*8, 9*) on the determination of mercaptans using a mercury(II) titration. The work dealing with the determination of mercury(II) is not yet published.

Isopropyl alcohol and water in the two immiscible phases were determined by gas chromatography using an F & M Model 700 instrument. The flow rate was 111 ml. per minute of helium, using a 2-meter 20% diisodecyl phthalate–Chromosorb column (60- to 80-mesh). The column temperature was 145° C. The retention time for water was 105 seconds and for isopropyl alcohol was 168 seconds. A calibration curve based upon volume per cent mixtures of alcohol and water was prepared and run using the same conditions as for the samples. Since the volume percentage of alcohol and water was measured in the solutions after extraction, corrections were made for the volume of salt present, measured by evaporation and weighing of the residue in each solvent layer.

RESULTS AND DISCUSSION

In this work, particular emphasis is given to systems in which the extracting solvent is itself salted out. For example, some interesting work has been done by Comar, who reports approximately 70 cases in which two-phase systems are formed with different salts. Attempts at practical uses are reported, such as the extraction of more than 95% of iron(III) chloride from an acetone–sodium chloride brine, and the purification of insulin and amino acids using two-phase acetone-salt-water systems (*2*). There are certain advantages in using such solvents. First, the solvents are usually just as insoluble in the saturated salt solution as conventional immiscible solvents. Secondly, the low molecular weight of the solvents increases the volatility, and makes possible ease of evaporation of the solvent. The fact that the solvent is miscible with water on dilution makes possible separation schemes based on subsequent metal ion or surface active agent precipitations without the presence of two phases.

In this study, acetone, dioxane, and isopropyl alcohol were investigated at 24° and 0° C. as extracting phases from saturated sodium chloride brines. The test systems used to evaluate the solvents were sodium lauryl sulfate detergent and iron(III) chloride solution. In these preliminary investigations, isopropyl alcohol was found to be the best extracting solvent. Acetone and dioxane were less suitable, in that order. The criteria for judging the effectiveness of the solvents were the distribution ratio of the test system in the solvent and the amount of nonpolar phase dissolving in the sodium chloride brine. Acetone lost 22% by volume, dioxane lost 50% by volume, but isopropyl alcohol gained 7.5% by volume, indicating that water was also extracted from the brine. The results measured at 0° C. were similar to those measured at room temperature. Dioxane solidifies at 0° C. in this system, and acetone loses 52% of its volume. The volume of isopropyl alcohol does not change measurably upon extraction at 0° C.

When equal volumes of isopropyl alcohol and saturated sodium chloride solution are combined, salt is precipitated, and two phases result. The upper phase increases in volume by 7.5%; the lower phase decreases by a similar amount. The upper and lower phases were analyzed for salt content by weighing. The isopropyl alcohol and water content of the two phases was analyzed by gas chromatography. The isopropyl alcohol and water content of the upper phase was 89 and 9.8%, respectively; salt content was 0.014 gram per ml. The alcohol and water content of the lower phase was 4.3 and 83%, respectively. The salt content of the liquid portion of the lower phase was 0.268 gram per ml. The weight of salt precipitated was 0.144 gram per ml. of lower phase after equilibration.

All detergents studied extracted very well in ranges up to 2×10^{-3} *M*, or, in the case of Benax-2A1, a 2 to 1000 dilution. Distribution ratios were greater than 100 in all cases. Most metal ions, however, were rather poorly extracted from saturated sodium chloride solution. Only gold(III), vanadium(IV), titanium(IV), iron(III), gallium(III), indium(III), tin(II), and vanadium(V) were extracted to a significant degree. Gold(III) extracted very well, having a distribution ratio of 125. The results of the extraction studies are presented in Table I. The effect of sodium lauryl sulfonate detergent on the extraction of metal ions is also included in the table. As can be seen, this detergent increases the extraction of traces of metal ions, but the increase is not large. Benax-2A1, an anionic detergent, increased metal ion extraction more than sodium lauryl sulfonate, possibly because it formed complexes with positively charged metal ion species, permitting their extraction as neutral complexes associated with a large nonpolar organic function.

Another interesting effect of detergents in these systems was the suppression of salt extraction. Sodium lauryl sulfate, the test system used for these studies, reduced the extraction of salt by approximately 17% when present in the aqueous phase at a concentration of 2×10^{-3} *M*. The salt content of the organic phase was reduced from 0.014 to 0.012 gram per ml. The water contents of the two phases were not analyzed in this series of experiments. The effect could be due to the replacement of extracted water by large detergent molecules, the displacement of salt molecules (hydrated) by detergent molecules, or a reduction in the polarity of the organic phase, making it less useful as an ionic extraction medium. The addition of hydrochloric acid to the extraction system did not increase the extraction of metal ions by isopropyl alcohol, and, in fact, depressed the extraction in many cases. The two exceptions were bismuth(III) and indium(III). The salt solutions used in this investigation were therefore maintained at neutral to slightly acidic pH. The high ionic strength of the solutions prevented the precipitation of metal hydroxides in all cases. In general, the extraction behavior of metal ions followed chloride extraction systems reported elsewhere (*17*).

The extraction of metal ions and organic substances, such as detergents, from brines can be considered as a form of salting-out solvent extraction. "Salting out," a term used in chemistry, refers to the addition of a salt to

Table I. Distribution Ratios of Metal Ions between Saturated NaCl Solution and Isopropyl Alcohol

Metal Ion	No Added Detergent	Benax-2A1, 2/1000 Dilution	Hyamine-1622, 2 × $10^{-3}M$	Sodium Lauryl Sulfate, 2 × $10^{-3}M$
Al(III)	0.29	0.32	0.22	0.00
Bi(III)	0.00	0.37	0.32	0.00
Cd(II)	0.10	0.11	0.12	0.11
Ce(III)	1.50	1.12	1.75	1.60
Co(II)	0.20	0.22	0.20	0.07
Cu(II)	0.08	0.31	0.22	0.15
Cr(III)	0.68	1.50	0.85	0.62
Fe(III)	1.50	2.07	1.90	0.90
Ga(III)	2.10	2.48	2.40	1.70
Au(III)[a]	125.0	126.0	268.0	113.0
In(III)	1.62	3.80	2.28	2.60
Pb(II)	0.00	0.00	0.00	0.00
Mg(II)[b]	0.17	...	...	...
Mn(II)	0.03	0.06	0.17	0.12
Hg(II)[c]	0.33	...	...	...
Ni(II)	0.49	0.43	0.30	0.30
Pt(IV)	0.30	0.55	0.31	0.30
Sb(III)	0.22	0.25	0.22	0.08
Sn(II)	1.60	2.35	2.60	2.60
Tl(I)	0.00	0.00	0.00	0.00
Th(IV)	0.80	1.10	0.90	0.30
Ti(IV)	6.80	7.10	6.90	6.00
U(VI)	0.61	1.20	1.15	0.80
V(IV)	10.60	15.54	15.00	16.00
V(V)	1.00	2.20	2.00	0.60
Zn(II)	0.13	0.25	0.86	0.24

[a] Results calculated using spectrophotometric measurements. [b] Analyzed by complexometric EDTA titration; 1.64 mmoles of Mg(II) salt used. [c] Determined using thioglycerol titrant and Thiomichler's ketone indicator according to method of Fritz and Palmer (*8, 9*).

a homogeneous system to cause the separation of a second phase. An example is the fractional precipitation of proteins using gradually increasing concentrations of ammonium sulfate. Many organic compounds which are normally miscible with water, such as *tert*-butyl alcohol (*12, 13*) and isopropyl alcohol (*11*), can be converted into two-phase immiscible systems by adding salts.

Several effects result from the addition of large amounts of salt to water (*7*). First, the ions in the anhydrous salts become hydrated, reducing the amount of water available to solubilize the solute to be salted out. Secondly, the addition of salts tends to decrease the dielectric constant of the medium, and encourages the formation of "ion pairs" which have a better chance of crossing the phase boundary of an immiscible pair of liquids than free ions. Thirdly, the increased ionic strength of strong salt solutions changes the activity coefficients of the various species in solution, influencing the extraction equilibrium. Fourthly, in case an extractable compound is formed with the salting-out agent, the mass-action effect of large amounts of salt tends to drive the compound into the extracting phase. Finally, the formation of complex ions can help or hinder the extraction of metal ions, depending on the ionic state of the complex (*17*).

The extraction of chloride complexes from solution depends on the formation of a neutral chloride complex, an ion association complex of a sodium or hydrogen ion with an anionic chloro complex, or finally the neutral ion pair formed when a large anionic detergent molecule is attached to a positively charged chloro cation of a metal. Since in our system the sodium chloride concentration in the isopropyl alcohol phase is $0.24M$, it is possible that sodium chlorometallate complexes can form and extract, most likely by a simple solubility process. Morrison and Freiser (*17*) report the extraction of many elements from hydrochloric acid into ether and other organic solvents. Correlating with their survey, we find that gallium(III), gold(III), iron(III), and tin(II) are well extracted. Titanium(IV), indium (III), vanadium(IV), and cerium(III) (as well as other rare earth elements, which display similar chemical properties) extract well from saturated sodium chloride brine. This latter series of elements is not predictable from the data of hydrochloric acid systems. Also, mercury(II), which is very well extracted by organic solvents from hydrochloric acid systems, is not extracted significantly from sodium chloride brines, possibly because of the formation of anionic chloride complexes of high charge, which do not form salts soluble in isopropyl alcohol.

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