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Chemistry of Metal Chloride Complexes in Aprotic Systems

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ABSTRACT

A study of metal chloride solubility in aprotic solvents has been initiated. These solvent systems have very low hydrogen ion activities and thus allow chloride ion activities which are much higher than those attainable in water. The high chloride ion activities can be generated by the dissolution of soluble salts, such as calcium chloride or sodium chloride, in the aprotic media. Metals that normally form aqueous-insoluble chlorides or exist as cations in aqueous solutions (e.g., Ag, Pb, Cd, or Au) may be readily dissolved in aprotic solvent systems as anionic chloride complexes or as solvation complexes. To understand such systems, we constructed ternary phase diagrams for dimethylsulfoxide-water-calcium chloride ($DMSO-H_2O-CaCl_2$) and $DMSO-H_2O-NaCl$ systems. These diagrams were used to establish the solution regions available for the solubilization of Pb, Ag, Au, Cd, Cu, Zn, and Al. Measurements of Pb and Ag solubilities in the $DMSO-H_2O-CaCl_2$ system gave concentrations as high as ~1.5 and ~0.9 M, respectively. Similar measurements showed concentrations of ~0.8, ~3.0, ~0.65, ~4.0, and ~0.85 M for Au, Cd, Cu, Zn, and Al, respectively. The concentrations of Pb and Ag in the NaCl system, ~0.45 and ~0.11 M, were much less than those obtained in the $CaCl_2$ system. Dissolution/precipitation steps, controlled by varying the ternary system composition, could lead to the development of useful methods for recovering, purifying, or separating various metal chloride compounds.

INTRODUCTION

In the applied field of hydrometallurgy, aqueous chloride chemistry is frequently employed in processes for the separation

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and recovery of metals from ores. In some cases, the formation of metal chloride anionic complexes is utilized in ion exchange or solubilization/precipitation steps in order to take advantage of the chloride complex chemistry to effect the separation of a desired metal. However, metals which do not form strong chloride complexes in aqueous chloride solutions cannot be processed by such techniques. Therefore, an experimental investigation was initiated to study nonaqueous solvent systems which could achieve higher chloride ion activities and find application in metal recovery processes.

In protic solvents such as water, the chloride ion activity attainable by the dissolution and dissociation of salts such as NaCl

$$NaCl = Na^+ + Cl^-$$

may be limited by the protonation reaction involving the water solvent

$$H_2O = H^+ + OH^-$$

$$H^+ + Cl^- = HCl$$

and metals such as lead, silver, gold, etc., which do not form strong chloride complexes, cannot be dissolved to useful concentrations in simple salt-water systems. Use of a suitable aprotic solvent could remove this restriction on chloride ion activity (1) and lead to the solubilization of metals by chloride complexation reaction as

$$MCl_y + xCl^- = MCl_{(x+y)}^{x-} ,$$

or by solvation

$$MCl_y + x(solvent) = M(solvent)_x^{y+} + yCl^- .$$

We have chosen to investigate dimethylsulfoxide (DMSO) systems since DMSO is a relatively innocuous and inexpensive reagent. It also has some physical properties similar to water and, thus, could be useful in practical hydrometallurgical appli-

cations. Only limited [illegible] DMSO-[illegible] potential application to silver chloride recovery (2) and for gold and silver separation (3) has been reported. The literature contains only limited basic information on the chemistry of metal chloride-DMSO-water systems. Phase diagrams for the DMSO-H_2O-NaCl and the DMSO-H_2O-$CaCl_2$ systems at 37°C have been published (4). Stability constants for a number of metal chloride complexes in DMSO have been calculated (1) and measured for silver (5) and for lead (6).

The research described in this paper was undertaken to deve-

MATERIALS AND METHODS

material obtained from the Fisher Scientific Company. Its water content was found to be in the range 0.1-0.2 wt % by Karl-Fischer titration. All of the salts ($CaCl_2$, NaCl, $PbCl_2$, $CdCl_2$, $CuCl_2$, $ZnCl_2$, $AlCl_3$) were ACS reagent-grade chemicals. Silver chloride was prepared in the laboratory by precipitation from a silver nitrate solution. Gold chloride (AuCl) was prepared from the metal by dissolution and evaporation techniques (7). Anhydrous salts were used where available. In cases where a anhydrous form was unobtainable, hydrated salts were dried at 100-200°C. Distilled water was passed through a Millipore reagent-grade water system to obtain pure water.

DMSO-H_2O mixtures with $CaCl_2$ or NaCl. These samples were mixed by rotation at 20 rpm in a constant-temperature water bath at 25 ± 0.1°C for 10-25 days to reach equilibrium. After equilibration, the saturated solutions were stored in the water bath until the solids settled. The clear solution was decanted for analysis. The metal chloride concentration was calculated from the metal

concentration value obtained by atomic absorption analysis of an aliquot of the saturated solution. The water content was determined by Karl-Fischer titration and the DMSO content was calculated by difference. All compositions of mixtures are given in weight percent.

For the solubility studies, DMSO-H_2O-$CaCl_2$ or NaCl mixtures were chosen in the solution region of the ternary phase diagram. Selected compositions were saturated with various metal chlorides at 25°C. The same experimental method was used for sample equilibration. For each metal chloride, a solubility curve with DMSO-H_2O mixtures was obtained as a base for evaluating the effect of added chloride (i.e., higher chloride ion activity) on the solubility. The saturated solutions were analyzed as described above.

RESULTS

The ternary phase diagram for DMSO-H_2O-$CaCl_2$ (Fig. 1) shows a useful solution region in the area bounded by 70-100% DMSO, 0-25% H_2O, and 0-6% $CaCl_2$. Attempts to identify the equilibrium solid phase(s) by extrapolation of the saturated solution–initial mixture tie-lines (8, 9) were unsuccessful. Parallel tie-lines, indicative of solid solution behavior, were obtained in some cases, while other tie-lines showed potential convergence in several regions. Several DMSO-H_2O-$CaCl_2$ solid compounds may exist; the shape of the saturated solution line suggests the possible existence of several invariant points, which would be consistent with several solid phases.

The solubility values for lead chloride in DMSO-H_2O and the DMSO-H_2O-$CaCl_2$ mixtures were typical of the results expected for the water–insoluble chlorides (Fig. 2). The highest saturated solution values for lead concentration (~1.5 M) were obtained with low water content and the highest concentration of added $CaCl_2$ (6%). The lead concentration shows an inverse relationship to the water content at all $CaCl_2$ concentrations. Silver chloride

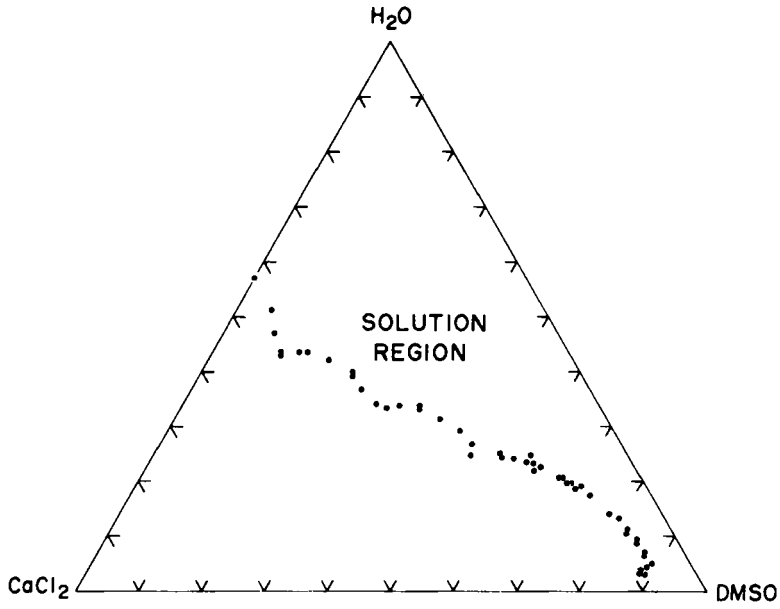

FIGURE 1. Ternary Phase Diagram for Dimethylsulfoxide-Water-Calcium Chloride at 25°C.

solubilized in DMSO-H_2O-$CaCl_2$ mixtures (Fig. 3) shows the same inverse relationship to water content. Concentrations of silver as high as ~0.9 M were obtained with 6% $CaCl_2$. The addition of $CaCl_2$ to the DMSO-H_2O mixtures gave a marked improvement in silver solubilization when compared with the DMSO-H_2O mixtures with no added $CaCl_2$. Gold solubilization (Fig. 4) was increased more than 2.5 times when 6% $CaCl_2$ was added to the DMSO as compared with 100% DMSO. The solubility of gold showed less of an inverse relationship to water than did the lead or silver chlorides. Cadmium concentrations as high as ~3.0 M were obtained in both DMSO-H_2O-$CaCl_2$ and DMSO-H_2O mixtures (Fig. 5). The cadmium concentrations appear to be higher in the DMSO-H_2O mixtures. Since previous work (2, 6) has shown that cadmium chloride is more soluble than $CaCl_2$ in DMSO, the addition of $CaCl_2$ to the DMSO-H_2O mixtures could be expected to decrease the cadmium solubility

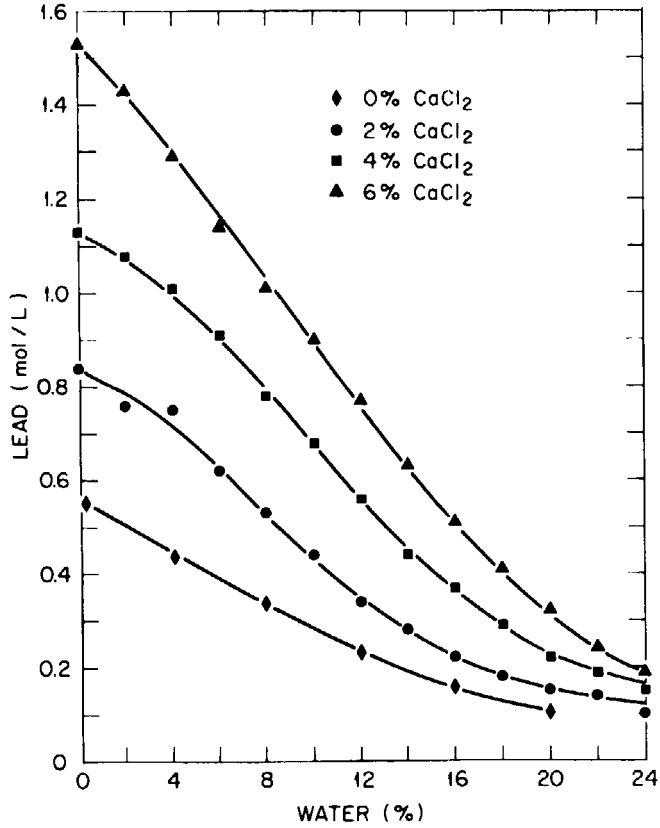

FIGURE 2. Lead Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

because of salting-out effects. The solubilization of copper chloride in DMSO-H_2O-$CaCl_2$ also shows an inverse relationship to water content (Fig. 6). Copper concentrations as high as ~0.65 M were obtained. However, the solubility of copper chloride in DMSO-H_2O mixtures was more directly related to the water content. Color changes occurred with the copper chloride solubilities in both DMSO-H_2O-$CaCl_2$ and DMSO-H_2O mixtures, suggestive of multiple complex formation or redox reactions. Concentrations in the range of ~3.0 to 4.0 M were obtained with zinc chloride (Fig. 7). The

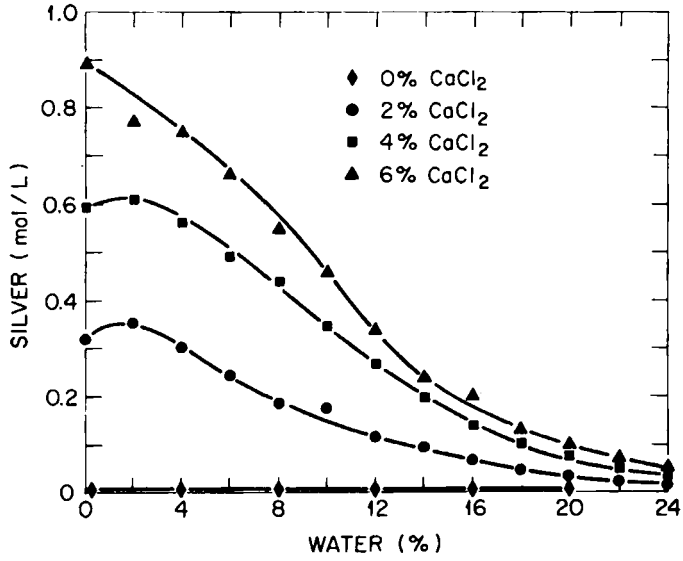

FIGURE 3. Silver Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

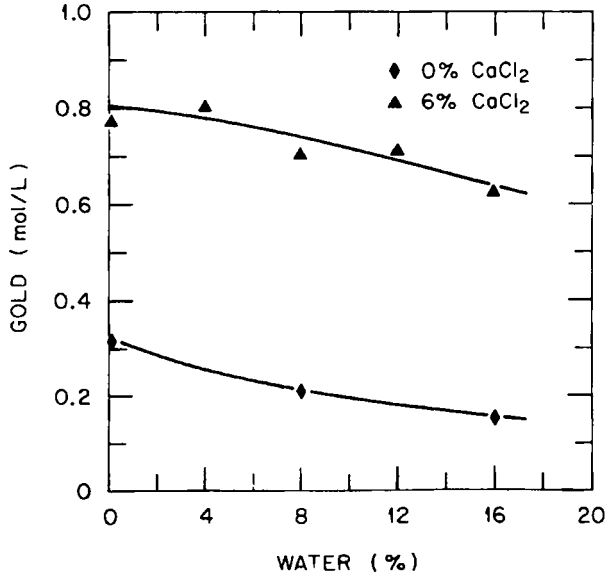

FIGURE 4. Gold Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

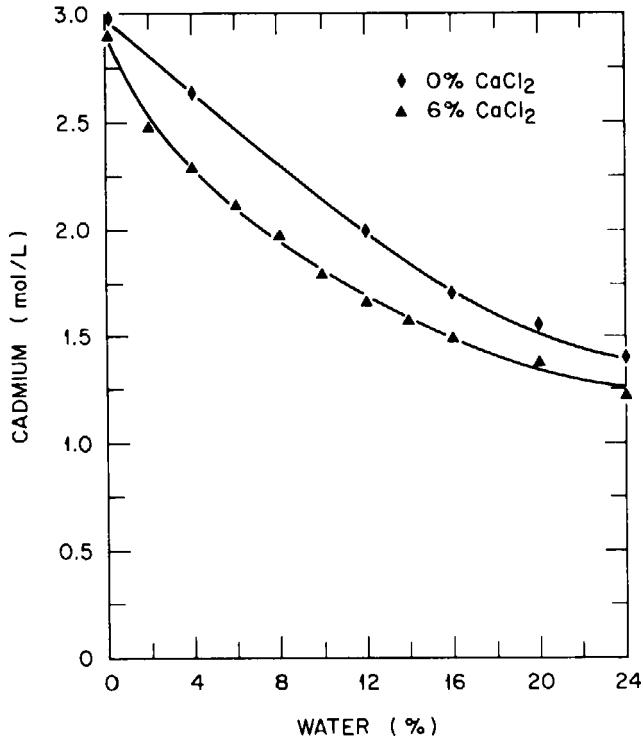

FIGURE 5. Cadmium Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

addition of $CaCl_2$ showed no significant increase or decrease in zinc concentration. The zinc concentrations appeared to increase slightly at higher water contents. The solubility of aluminum chloride (Fig. 8) was directly related to the water contents of the DMSO-H_2O and DMSO-H_2O-$CaCl_2$ mixtures. No significant difference was observed between the sample concentrations with added $CaCl_2$ and those with no $CaCl_2$ added.

The ternary phase diagram for DMSO-H_2O-NaCl (Fig. 9) shows a smaller solution region than that obtained with $CaCl_2$. Because the solution region is restricted and NaCl is less soluble, the solubilities of some metal chlorides are much lower in the

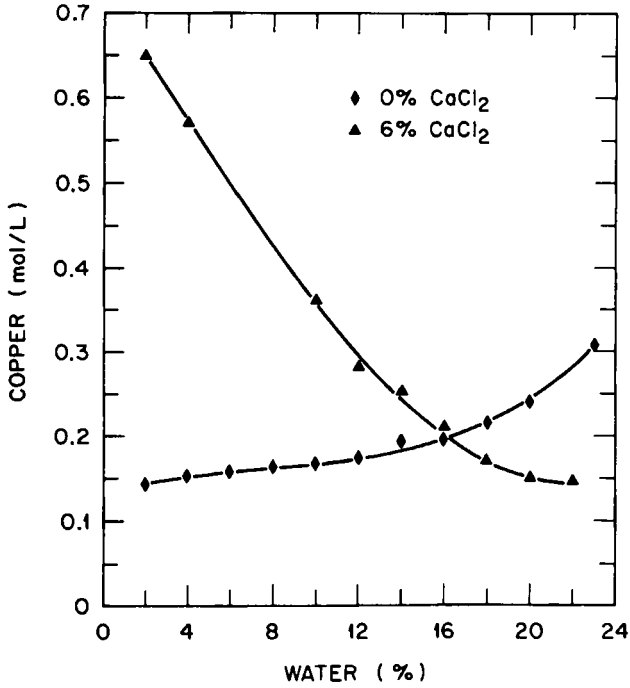

FIGURE 6. Copper Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

DMSO-H_2O-NaCl than in the DMSO-H_2O-$CaCl_2$ system. The solubilities of lead chloride and silver chloride shown in Figs. 10 and 11, respectively, demonstrate this. To obtain 1% NaCl, the water content of the mixture was at 8%; for 3% NaCl, it was 24%; and for 5% NaCl, it was 32%. The solubilities of lead and silver chlorides were very low when the water content was 20% or more in this ternary system.

DISCUSSION

Our ternary phase diagrams for the DMSO-H_2O-$CaCl_2$ and DMSO-H_2O-NaCl systems are the first reported at 25°C. The position of the saturated solution line is in general agreement with

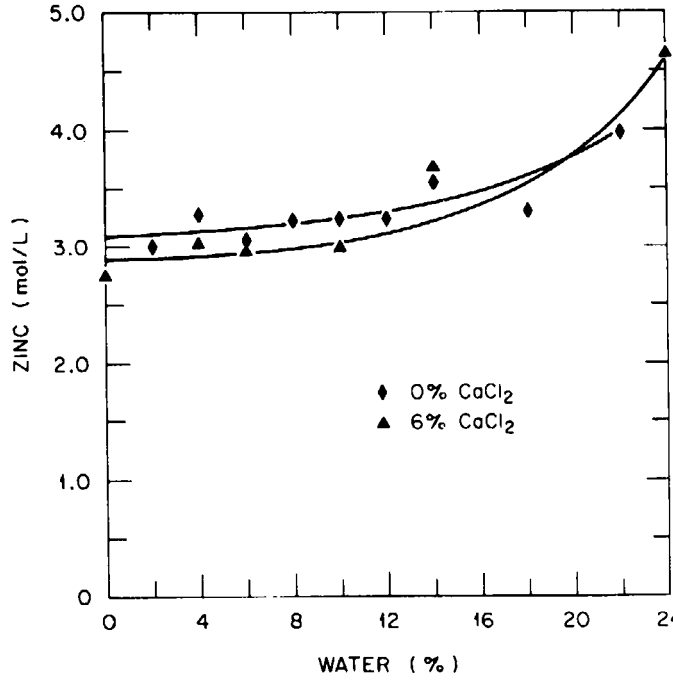

FIGURE 7. Zinc Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

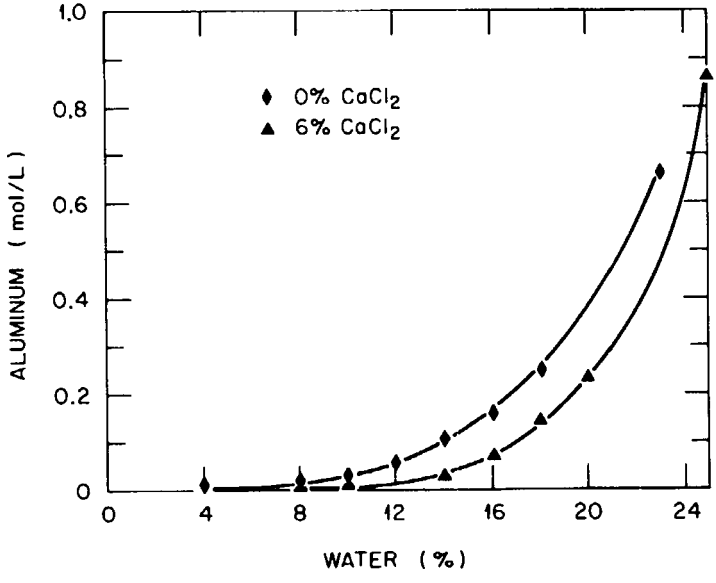

FIGURE 8. Aluminum Solubility in DMSO-H_2O-$CaCl_2$ Mixtures at 25°C.

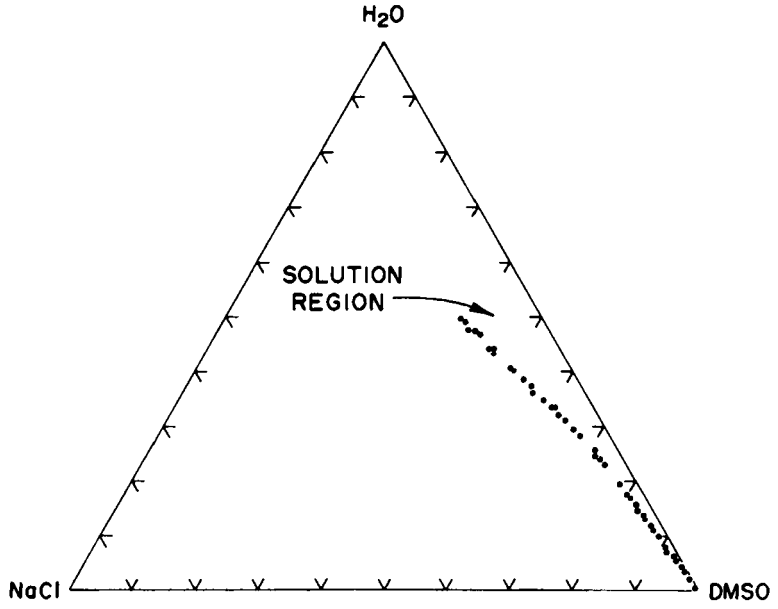

FIGURE 9. Ternary Phase Diagram for Dimethylsulfoxide-Water-Sodium Chloride at 25°C.

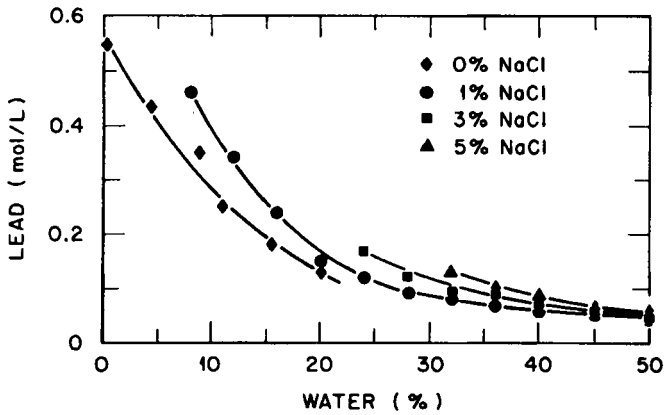

FIGURE 10. Lead Solubility in DMSO-H_2O-NaCl Mixtures at 25°C.

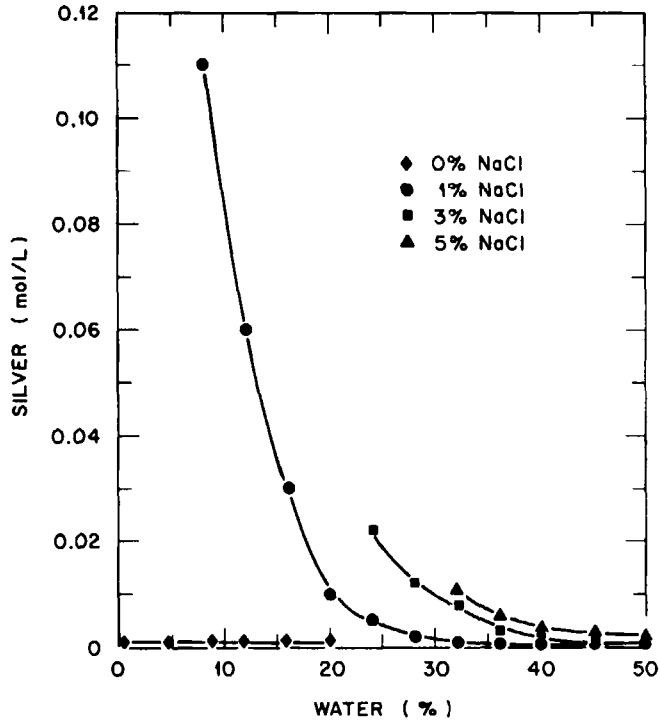

FIGURE 11. Silver Solubility in DMSO-H_2O-NaCl Mixtures at 25°C.

published phase diagrams at 37°C (4). Continuous solid solution behavior in the saturated region was observed in our work with the DMSO-H_2O-NaCl system, in agreement with published results (4). We were unable to identify the several possible equilibrium solid phases that may be present in the DMSO-H_2O-$CaCl_2$ system and are concerned that the previously published phase diagram (4) may not adequately describe the saturated region since it shows no evidence of the well-known hydrated forms of $CaCl_2$.

Dissolution of metal chloride compounds in the solutions selected from the solution region of these ternary systems can occur primarily by three reactions: solvation, chloride complexation, or hydration. In solvation reactions, the metal ion is

surrounded by a DMSO solvation layer and solubilized as a metal-DMSO moiety by reactions such as

$$MCl_y + xDMSO = M(DMSO)_x^{y+} + yCl^- \ .$$

In reactions of this type, the solubility of the metal chloride would be expected to be inversely related to chloride ion activity or H_2O concentration. In chloride complexation reactions of the type

$$MCl_y + xCl^- = MCl_{(x+y)}^{x-} \ ,$$

the solubility of the metal ion should be directly related to the chloride ion activity and inversely related to the H_2O content, due to the competing protonation reactions

$$H_2O = H^+ + OH^- \ ,$$

$$H^+ + Cl^- = HCl \ .$$

Of course, metal chlorides could also be solubilized in the water content of the systems (hydration reaction); in this case, the solubility of the metal chloride should be inversely related to the DMSO content.

Examples of all three types of behavior can be seen in the metal chloride solubility data. Silver chloride appeared to be solubilized only by complex formation (Fig. 3); no suggestion of solvation of AgCl was observed. Synnott and Butler (5) have measured the formation constant for $AgCl_2^-$ in DMSO as a function of H_2O concentration and found high values at low H_2O contents; thus, it seems reasonable to suggest that silver dissolves according to the equilibrium

$$AgCl + Cl^- = AgCl_2^- \ .$$

Lead chloride and gold chloride showed similar increased solubility with increased chloride concentration, except that appreciable solubility due to solvation can also be seen (Figs. 2, 4) in the absence of added $CaCl_2$. Lead chloride has been studied in DMSO, and the complexes $PbCl_2^-$ and $PbCl_3^{2}$ were inferred (6).

Presumably, similar complexes are being solubilized in our experiments. No literature references to the stability of gold chloride complexes in DMSO were identified.

Different behavior was observed for cadmium chloride and zinc chloride (Figs. 5 and 7). Both were quite soluble in the absence of added chloride, and their solubilities decreased slightly as $CaCl_2$ was added to the system. Thus, for these elements, no evidence of chloride complexation was obtained and solubility appeared to be effected solely by solvation and to be repressed by added $CaCl_2$ due to salting-out effects. The behavior of copper chloride (Fig. 6) was complicated, and the formation of variously colored solutions suggests the presence of multiple complexes and also possible reaction with the DMSO to form reduced copper (1). Aluminum chloride appeared to be soluble only in the water content of the systems (Fig. 8).

Additional research is under way to explore the effect of temperature on the solubilities of some of these metal chlorides and to construct the ternary phase diagram for the DMSO-H_2O-NH_4Cl system. Also, measurements of pertinent physical constants are being initiated.

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