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10 to 20% the amount of potassium coprecipitated up to a Triton-X 100 concentration of 0.3% in all treatments except the reverse precipitation with no digestion and the hot precipitation with digestion. Since the maximum concentration of molecularly dispersed Triton-X 100 occurs in a 0.3% solution and the effect of added KCl is to increase the micelle formation, this is in the region where the maximum concentration of Triton-X 100 should be found. This suggests that a surfactant can compete with potassium acting as counter ion in seeking surface sites on BaSO₄ precipitates. Although the least coprecipitation of potassium occurs with reverse precipitation, the coprecipitation of anions is important here. The effect of Triton-X 100 on anion coprecipitation has not yet been determined.

Future experiments should investigate two avenues of approach, first the reverse precipitation procedures in the presence of surface active agents and second the effect of other surface active agents, including both ionic and nonionic surfactants, on coprecipitation with BaSO₄.

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Cation Exchange Equilibria in Mixed Solvents Sorption Characteristics of Common Metals from Water-Dimethyl Sulfoxide-Hydrochloric Acid Mixed Solvent

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Abstract. The systematic study of sorption of Ca, Cd, Co(II), Cu(II), Fe(III), Hg(II), In(III), La, Mn, Ni(II), Th(IV), Pb, Yb, U(VI), and Zn by Dowex 50 x 8 cation exchange resin from dimethyl sulfoxide-water-hydrochloric acid mixed solvent is presented. The sorption characteristics are much the same as those found for acetone-water-hydrochloric acid mixed solvent. Major differences occur in the case of Fe(III), Ca, Mg, and Pb. Many useful separations involving these elements are indicated.

Over the past few years, interest in mixed solvent systems for ion exchange separations has increased significantly. We noted that the water-dimethyl sulfoxide mixed solvent system had not

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been studied, in spite of several obvious advantages provided by this system. For one, dimethyl sulfoxide (DMSO) has a strong tendency to solvate metal ions, and the solubility of inorganic salts is correspondingly high (1). Salts of lead and silver, which ordinarily precipitate from aqueous hydrochloric acid or hydrobromic acid solutions, are reasonably soluble in water-DMSO mixed solvent. The separation of constituents of lead base materials appeared likely without prior removal of lead or use of strong complexing reagents. Another advantage is that DMSO is a non-flammable solvent, in contrast to the alcohols or acetone, and should lend itself to industrial application. Dimethyl sulfoxide is now commercially available in high purity, the toxicity is low, and the odor is not unpleasant, so it is not an objectionable solvent to work with.

In regards to the ion exchange behavior in water-DMSO mixed solvent, one would expect the sorption characteristics to be somewhat the same as in water-acetone mixed solvent. The sorption of a number of metals from water-acetone-HCl-mixed solvent by cation exchange resin has been reported by Fritz and Rettig (2). These investigators found that the sorption of many metals increased at first as the acetone content increased, then decreased sharply. No reason was given for the unusual increase, but the decrease was attributed to complex formation with HCl in the lower dielectric media. The purpose of this paper is to contrast the sorption by cation exchange resin from water-DMSO-HCl and water-acetone-HCl mixed solvents, to point out the separations that appear to be unique to the DMSO mixed solvent system, and to interpret the anomalous increase in distribution coefficients at low organic solvent contents.

EXPERIMENTAL WORK

Solutions of metal perchlorates, (G. F. Smith Chem. Co.), used in the measurement of distribution coefficients, were approximately 0.05M and were standardized by titration with standard (ethylenedinitrilo) tetraacetic acid disodium salt (EDTA) using appropriate buffer and indicator systems. EDTA was standardized against standard zinc perchlorate (prepared from metallic zinc) using pyridine buffer and Naphthylazoxine indicator (3). The analytical methods for metal analyses are outlined in Table 1. The presence of DMSO had no adverse effect on the titrations.

Solutions of 0.50 M HCl in water-DMSO were prepared on a volume percent basis at increments of 10% DMSO. The volume contraction for this particular system is small. Thus, the concentrations of HCl were not corrected for this effect.

Dowex 50 x 8 ion exchange resin, 100-200 mesh in the chloride form, was used in the measurement of distribution coefficients. The resin was first backwashed with distilled water to remove the very fine particles, treated with 3 M HCl, then washed with distilled water until a negative chloride test was obtained. The resin was air dried and stored in a stoppered bottle.

Distribution coefficients were determined in the following manner. To one gram of air dried resin in a 125 ml glass stoppered Erlenmeyer flask was added 4.0 ml metal perchlorate solution and 50.0 ml of the appropriate DMSO-water-HCl solution. The flask was stoppered and shaken for 24 hours. The mixture was allowed to settle, then an aliquot withdrawn for metal analysis. The water content of the resin was determined by drying at 110°C and the mass distribution coefficients were calculated on a dry weight basis.

Table 1. Analytical Procedures

Metal ion	Titration method	pH	Buffer	Indicator
Ca ⁺⁺	EDTA, B(Zn)	10	NH ₃ -NH ₄ Cl	Erio BT
Cd ⁺⁺	EDTA	6	Pyridine	NAS
Co ⁺⁺	EDTA	6	Pyridine	NAS
Cu ⁺⁺	EDTA	6	Pyridine	NAS
Fe ⁺⁺⁺	EDTA, B(Zn)	6	Pyridine	NAS
Hg ⁺⁺	EDTA, B(Zn)	10	NH ₃ -NH ₄ Cl	Erio BT
In ⁺⁺⁺	EDTA, B(Zn)	6	Pyridine	NAS
La ⁺⁺⁺	EDTA	6	Pyridine	NAS
Mg ⁺⁺	EDTA	10	NH ₃ -NH ₄ Cl	Erio BT
Mn ⁺⁺	EDTA	10	NH ₃ -NH ₄ Cl	Erio BT
Ni ⁺⁺	EDTA	6	Pyridine	NAS
Th ⁺⁺⁺⁺	EDTA, Z(Cu)	6	Pyridine	NAS
Yb ⁺⁺⁺	EDTA	6	Pyridine	NAS
UO ⁺⁺	Ceric Sulfate	-	-	Ferroin
Zn ²⁺⁺	EDTA	6	Pyridine	NAS

The time required to reach equilibrium in the sorption of magnesium from 88% DMSO-water-HCl mixture is less than one hour. Presumably, the time required of other metals at all DMSO contents would be on the order of one hour. A twenty four hour equilibration was allowed for each metal, however, in order to insure an equilibrium measurement.

RESULTS AND DISCUSSION

A summary of the mass distribution coefficients for a number of common metals at varying DMSO contents at 0.46 M HCl is given in Table 2. Here, as in the acetone-water-HCl mixed solvent, pronounced sorption maxima occur. Since DMSO is known to dehydrate metal ions, and in some cases displace coordinated ligands from a metal ion (4, 5, 6), it is very likely that the increase in mass distribution coefficients is the result of the displacement of coordinated chloride ligands. The decrease in D_{mass} values is due to chloro-complex formation as

Table 2. Distribution coefficients of Metals for Dowex 50 x 8 Ion Exchange Resin, DMSO-Water- 0.46 M HCl

Metal ion	Per cent Dimethyl Sulfoxide										
	0.0	9.3	18.5	27.8	37.0	46.3	55.6	64.8	75.0	83.3	88.0
Ca ⁺⁺	161	164	210	217	256	391	558	402	398	402	212
Cd ⁺⁺	8	8	5	11	4	0	0	0	0	0	0
Co ⁺⁺	90	95	103	121	144	101	170	135	106	29	6
Cu ⁺⁺	86	88	94	78	98	75	57	31	26	3	4
Fe ⁺⁺⁺	367	820	1700	1710	1710	1685	1690	1675	512	220	124
Hg ⁺⁺	27	1	1	2	1	3	1	3	1	1	3
In ⁺⁺⁺	8	20	17	17	19	22	8	2	5	2	14
La ⁺⁺⁺	Lanthanum absorbed strongly by the resin										
Mg ⁺⁺	94	84	85	84	92	101	149	133	131	121	121
Mn ⁺⁺	91	93	92	91	115	117	113	120	92	59	25
Ni ⁺⁺	109	97	165	133	155	158	154	164	185	99	77
Th ⁺⁺⁺⁺	Thorium adsorbed strongly by the resin										
Yb ⁺⁺⁺	500	640	747	505	1035	1704	2520	3150	2520	3150	2520
UO ⁺⁺	137	357	737	675	682	618	592	341	250	140	114
Zn ²⁺⁺	90	91	76	60	29	10	18	14	9	0	0
Pb ⁺⁺	50	61	52	38	42	22	14	7	3	0	0

evidenced by the change in color of Co(II) and Ni(II) at high DMSO contents, and the fact that DMSO solvated salts of the type $M^{n+} Cl_n \cdot x DMSO$ and $M(DMSO)_4 Cl_2 MCl_4$ are known to form in DMSO (6, 7, 8).

The sorption of iron, copper, cadmium, cobalt, and lead from 1M HCl is summarized in Table 3. The increase in HCl con-

Table 3. Distribution Coefficients of Metals for Dowex 50 x 8 Ion Exchange Resin, DMSO-Water-0.92 M HCl

Metal ion	0.0	9.3	18.5	27.8	37.0	46.3	55.6	64.8	75.0	83.3
Co ⁺⁺	7	7	7	11	20	10	21	18	9	0
Cd ⁺⁺	Cadmium not absorbed by the resin									
Cu ⁺⁺	9	9	8	6	4	0	0	0	0	0
Fe ⁺⁺⁺	37	86	87	88	123	125	128	112	62	49
Pb ⁺⁺	4	0	0	0	0	0	0	0	0	0

centration leads to lower D_{mass} values as would be expected from greater complex formation. The change in D_{mass} values for iron and cobalt, Figure 1, is approximately the same at all solvent compositions. This makes the selection of conditions for separations somewhat easier from preliminary data.

For the most part, the behavior of the metals is about the same as in acetone-water-HCl solvent. There are some notable exceptions, though. For one, ferric ion shows a large increase in D_{mass} as the DMSO content is increased, while there is no increase in acetone mixed solvent. This increase is also found at higher chloride concentrations. Since the distribution coefficients are large over the entire range of solvent compositions, the separation of many metals from iron appears possible. Iron may be stripped from the resin by treatment with strong HCl in essentially pure DMSO.

Another difference between sorption from DMSO and acetone mixed solvents is evident by comparison of the uptake of calcium and magnesium. Figure 2 shows that the difference between the two metals is accentuated by the addition of DMSO. The separation factor, D_{Ca}/D_{Mg} , in 55.6% DMSO is more than twice that in aqueous 0.5M HCl. The addition of acetone apparently reduced the difference between these elements, for they have nearly identical D_{mass} coefficients in 80-90% acetone. Assuming the distribution coefficients are proportionately lowered by an increase in HCl content, the separation of calcium from magnesium in DMSO mixed solvent should be possible.

Another major difference between DMSO and acetone mixed solvent arises from the solubility of sparingly soluble chloride salts in DMSO. Lead chloride is quite soluble in DMSO-water-HCl solvent, and reference to Tables 2-3 show that many separations involving lead are possible. Silver chloride is sufficiently

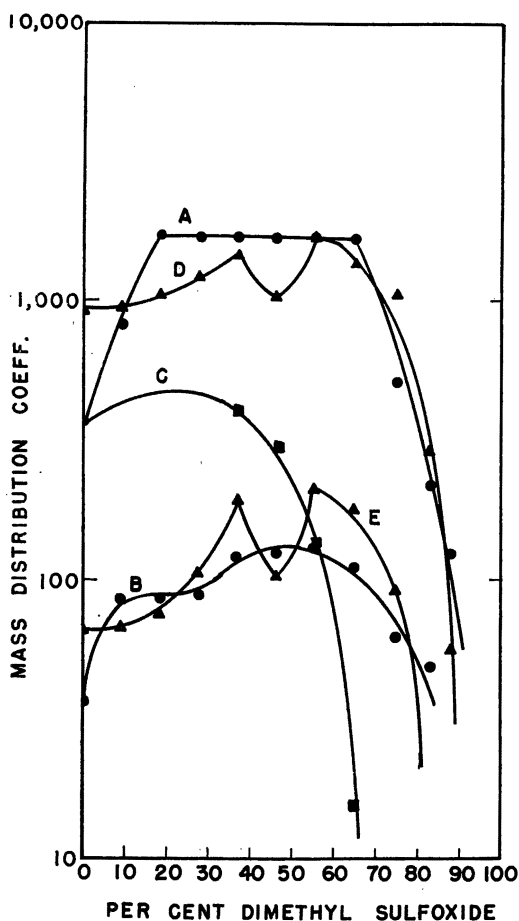


Fig. 1. Variation of distribution coefficients of iron and cobalt with mixed solvent composition. Dowex 50 x 8 ion exchange resin, DMSO-water-HCl mixed solvent.

- A. Iron (III), water-DMSO-0.46 M HCl
- B. Iron (III), water-DMSO-0.92 M HCl
- C. Iron (III), water-acetone-0.5 M HCl
- D. Cobalt (II), water-DMSO-0.46 M HCl, x 10
- E. Cobalt (II), water-DMSO-0.92 M HCl, x 10

soluble at high DMSO contents to carry out ion exchange separations. Further work is in progress to determine distribution coefficients for silver, and to determine conditions for separation of the constituents of lead and silver base alloys.

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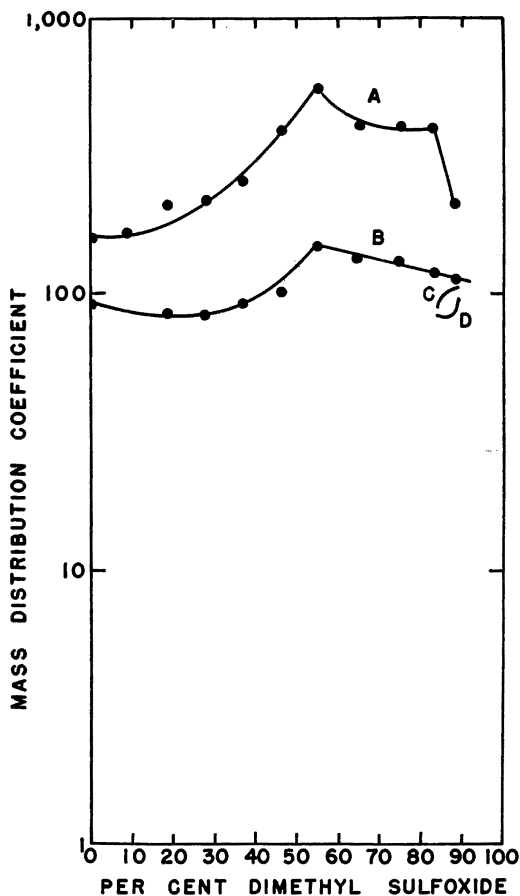


Fig. 2. Variation of distribution coefficients of calcium and magnesium with mixed solvent composition. Dowex 50 x 8 ion exchange resin, DMSO-water-HCl mixed solvent.

- A. Calcium, water-DMSO-0.46 M HCl
 B. Magnesium, water-DMSO-0.46 M HCl
 C. Calcium, water-acetone-0.5 M HCl
 D. Magnesium, water-acetone-0.5 M HCl

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