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ANION EXCHANGE BEHAVIOR AND SEPARATIONS OF METAL IONS IN DIMETHYL SULFOXIDE-METHYL ALCOHOL-HYDROCHLORIC ACID SYSTEMS

by

Marcia Lehoczky Gillette

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INTRODUCTION

Anion exchange column chromatography has been an important analytical tool for slightly more than twenty years. The first significant use of the technique was reported in 1945 by Sussman et al. (1) and involved the separation and recovery of metals. What undoubtedly represents the most comprehensive and exhaustive consideration of the method is the work of Kraus and Nelson (2,3) who studied, beginning in 1948, the behavior of metal ions on Dowex 1x10, a strongly basic anion exchange resin. Distribution coefficients were measured for almost every metal over a wide range of hydrochloric acid concentrations (0.1 - 12 M), and additional studies were made of selected elements (primarily the 4th and 5th groups of the transition metals) in combined hydrochloric acid-hydrofluoric acid systems. Included in this work is a brief description of metal ion behavior in nitrate, sulfate, and several other systems. Although the number of possible ligand combinations is large, the flexibility and versatility of the chloride system combined with the large number of metals which form chloride complexes of varying stabilities (as contrasted to metal complexes with other ligands) makes this the most analytically useful system available.

Since the work of Kraus and Nelson a great many articles have been published describing new systems and separation schemes employing anion exchange column chromatography. The technique is reviewed biennially in "Analytical Chemistry" and two books are available as references which describe both the theoretical and technical aspects of the method (4,5).

A relatively new development in the field of anion exchange chromatography is the use of organic solvents to replace either partially or completely the totally aqueous systems. It was found generally that the addition of organic solvents to a metal-ligand system effectively enhances the formation of metal-ligand complexes in the system. This discovery led to a re-examination of anion exchange using ligands (e.g. bromide, nitrate, sulfate) which had not previously been of much interest owing to the relatively small number of metals which complex strongly enough with them to be retained by an anion exchanger. The most commonly studied organic solvents were aliphatic alcohols, acetone, dioxane, and the lower carboxylic acids.

The unusual solvating powers of dimethyl sulfoxide render it of interest as an organic solvent to be used in conjunction with anion exchange chromatography. The high solubility of many metal salts in pure dimethyl sulfoxide and in dimethyl sulfoxide containing only small amounts of acid make it a potentially useful means of including many metals in an anion exchange scheme at low acid concentrations which would normally not be stable under similar aqueous conditions. Thus the combination of the solvating powers of dimethyl sulfoxide and the versatile hydrochloric acid system make a potentially interesting and useful system for use with anion exchange column chromatography.

It was the purpose of this research to explore the effect of dimethyl sulfoxide on the anion exchange behavior of many metals in a mixed solvent system containing methyl alcohol and hydrochloric acid. From the observed behavior it was possible to draw conclusions regarding the mechanistic effect of dimethyl sulfoxide in systems such as these. With the inclusion of studies of the effects of water and of increased acid concentration on the behavior of metals, many useful anion exchange separations based on the dimethyl sulfoxide-methyl alcohol-hydrochloric acid system were devised. The incorporation of silver(I) and lead(II) into separation schemes carried out in systems containing as little as 0.6<u>M</u> chloride exemplify the usefulness of dimethyl sulfoxide as a nonaqueous solvent for anion exchange. The rapidity and completeness of separations in the dimethyl sulfoxide-methyl alcohol-hydrochloric acid system coupled with the simplicity of its application make this the method of choice for the resolution of many metal ion mixtures.

USE OF ORGANIC SOLVENTS IN ANION EXCHANGE CHROMATOGRAPHY

Survey of the Literature

Among the earliest references to the use of nonaqueous solvents with ion exchange chromatography is in the work of Katzin and Gebert (6) where the sorption of hydrochloric acid, lithium chloride, lithium nitrate, cobalt(II) nitrate, copper(II) chloride, and nickel(II) nitrate onto chloride- and nitrate-form anion exchange resins from acetone solutions is reported. This behavior is contrary to what would be observed in equivalent aqueous systems and some speculation regarding a mechanism and factors affecting absorption is offered. Since that time a great deal has been published regarding the effects and use of organic solvents in anion exchange chromatography. This survey is divided into four groupings: papers of a general nature, papers dealing with nonaqueous hydrochloric acid systems, papers concerned with nonaqueous nitric acid systems, and finally papers describing nonaqueous sulfuric acid systems. Within each grouping the papers are referred to in chronological order.

Of a surveyal nature is the work of Korkisch *et al.* (7) regarding the anionic behavior of uranium(VI) in ethanolic solutions of hydrochloric acid, nitric acid, and sulfuric acid on Dowex 1 resin, and (8) describing the anionic behavior of thorium(IV), zirconium(IV), and titanium(IV) in the same resin and solvent systems. Later Korkisch (9,10,11) studied the anion exchange behavior of uranium(VI), thorium(IV), and some other elements on Dowex 1 resin in hydrochloric acid, nitric acid, and sulfuric acid solutions containing aliphatic alcohols, ketones, ethers, acetone, organic acids, and chlorinated derivatives of acetic acid. Included in the study is a discussion of some of the theoretical principles governing the behavior observed in the use of nonaqueous solvents in anion exchange. Urubay _et_ _al_. (12) described the adsorption behavior of uranium(VI), thorium(IV), iron(III), and aluminum(III) on Dowex 1 resin from mixtures of diethyl ether, diisopropyl ether, and dioxane with hydrochloric acid and nitric acid. Based on their distribution data they developed successful separation methods for these elements. Finally, Marple (13) studied the adsorption of uranium(VI) and thorium(IV) on Dowex 1 resin from alcoholic hydrochloric acid and nitric acid solutions and related the results to a suggested mechanism of adsorption.

The most completely studied metal-ligand system in terms of its anionic behavior in nonaqueous solvents is the chloride system. One of the earliest papers published describes the work of Burstall _et al._ (14) involving an ion exchange process for the recovery of gold(III) from cyanide solutions. They found that contrary to its practically irreversibly high sorption from aqueous chloride solutions onto anion exchange resins, a large variety of organic solvents elute gold rapidly and efficiently from the resin. Systematic study indicated that the optimum elution conditions for gold from its cyanide complex on Amberlite IRA-400 anion exchange resin utilized an eluent containing acetone with 5% hydrochloric acid and 5% water.

In 1957 Yoshino and Kurimura (15) studied the behavior of zinc(II) and copper(II) in organic solvent mixtures of hydrochloric acid. From the differences in behavior observed with the addition of organic solvents and with changes in the amount and nature of the organic solvent they offered an explanation of the observed solvent effects. At the same time the anion exchange behavior of aluminum(III), zinc(II), and copper(II) was studied from methanolic and ethanolic mixtures of hydrochloric acid by Kojima (16). The study was later broadened (17) to include an examination of iron(III), cobalt(II), and nickel(II) behavior in the same solvent systems. A suitable separation of iron, cobalt, and nickel, and of iron, cobalt, nickel, copper, and zinc using anion exchange resin with a methanolic eluent containing a low concentration of hydrochloric acid was devised. Berg and Truemper (18) report the separation of zinc(II), cadmium(II), and mercury(II) using 0.01M hydrochloric acid containing from 10 to 25% methyl alcohol.

In 1961 Wilkins and Smith (19) investigated the ternary system of ethyl alcohol-water-hydrochloric acid for the anion exchange separation of elements which have low adsorption coefficients in aqueous hydrochloric acid solutions. The separation of manganese(II) from nickel(II) and calcium(II), and the separation of yttrium(III) from scandium(III) was accomplished. The behavior of yttrium(III), neodymium(III), and lanthanum(III) on Amberlite IRA CG-400 resin was studied in dilute hydrochloric acid solutions containing ethyl alcohol by Edge (20). Rare earths are not adsorbed by strong-base anion exchange resins at any concentration of hydrochloric acid in aqueous systems but these representative elements were taken up by the resin from 1M hydrochloric acid containing 80% ethyl alcohol. Fritz and Pietrzyk (21) reported the distribution coefficients of many metal ions between Dowex 1 resin and mixtures of methyl alcohol, ethyl alcohol, and isopropyl alcohol with varying aqueous concentrations of hydrochloric acid. A number of successful column separations of metal ion mixtures were developed by these authors. Finally, a great deal of work was reported by Korkisch *et al*. (22-27) on the behavior of uranium(VI), thorium(IV), and vanadium(V) in organic solvents containing hydrochloric acid.

A considerable amount of study has also been devoted to nitric acid-organic solvent systems in connection with anion exchange chromatography. Edge (28) described the behavior of yttrium(III), neodymium(III), and lanthanum(III) in dilute nitric acid solutions containing ethyl alcohol on Dowex 1 resin, and Faris and Warton (29) studied and separated the rare earths, yttrium(III), and scandium(III) in methanolic solutions of nitric acid on anion exchange resins. Again Korkisch and co-workers have thoroughly studied the behavior of uranium(VI) in alcoholic nitric acid solutions (30,31) as well as the behavior of thorium(IV) (31-33), bismuth(III) (31), and the rare earths (34) in these systems. Separations have been proposed for many of these elements.

Fritz and Waki (35), in 1963, published an anion exchange separation method for magnesium(II) and calcium(II) using a solution of 0.5M nitric acid in 90% isopropyl alcohol as an eluent. Soon thereafter, an anion exchange method for the separation of calcium(II) and strontium(II) was developed by Fritz *et al*. (36) using a mixed solution of 0.25M nitric acid and 95% methyl alcohol as an eluent.

Marple (37) investigated the sorption of lead(II) on anion exchange resin from nitric acid-isopropyl alcohol-water mixtures. In his work, Marple followed polarographically the formation of lead nitrate complexes and reported successive formation constants of the first and second complexes in various concentrations of isopropyl alcohol. From these data it was possible to correlate the distribution coefficients of lead with the mole fraction of isopropyl alcohol in the solvent mixture. Fritz and Waki (38,39) published a two-part study on the effect of organic solvents on complexes in ion exchange with specific work done on silver(I), magnesium(II), and calcium(II) nitrate complexes in aqueous isopropyl alcohol. Fritz and Greene (40,41) have studied and developed anion exchange separation methods for the rare earths from other metal ions (especially from bismuth, lead, and thorium) using 1.5M nitric acid and 85% isopropyl alcohol as an eluent.

Finally, an anion exchange procedure for separating the rare earths has been developed by Alstad and Brunfelt (42) using Dowex 1 resin and an acetone-nitric acid system.

Only two papers have been published in which nonaqueous solvents were used in a sulfuric acid system for anion exchange chromatography. Edge (43) studied the behavior of yttrium(III), neodymium(III), praseodymium(III), and lanthanum(III) in dilute sulfuric acid solutions containing ethyl alcohol and found that the system of 0.01N sulfuric acid and 80% ethyl alcohol permitted microseparations of neodymium from lanthanum, of yttrium from lanthanum, of neodymium from yttrium, and of praseodymium from yttrium all using very slow flow rates. Janauer and Korkisch (44) investigated the anion exchange behavior of uranium(VI) and thorium(IV) in sulfuric acid solutions containing aliphatic alcohols. They found that both elements were highly retained in these systems by Dowex 1 resin.

Theoretical Effects of Organic Solvents on Anion Exchange Chromatography

The theoretical aspects of organic solvent effects in anion exchange chromatography have been explored to a much lesser extent than have the practical advantages. One of the first attempts at characterizing the mechanism of adsorption was made by Katzin and Gebert (6). They described the adsorption of several salts from an acetone solution as the disappearance of the entire molecule from the liquid phase rather than as ions being exchanged. They suggested that at least three factors exert important influences on the mechanism of adsorption: the nature of the anion associated with the cation in solution, the nature of the anion associated with the resin, and the water content of the starting resin or in the total system, and concluded that the salts were taken up as complex anions.

The composition of resin and solution phases of polystyrene-matrix ion exchange resins in mixed solvent systems has been determined on numerous occasions (45-50). Davies and Owen (49) reported that the resin phase in such systems is predominately aqueous and the solution phase predominately organic, thus establishing a two-phase situation ideally suited for partition chromatography. Partitioning effects were therefore thought to enhance the normal separation, and the results of Katzin and Gebert were re-interpreted as being due to partitioning effects.

In all composition studies it was found that resins absorb characteristic amounts of solvents from a mixed system. The absorption was found to be a function of the divinyl benzene content of the resin, the dielectric constant of each solvent, and the ionic form of the resin. An equilibrium coefficient for the distribution of two solvents between a solution and resin phase was defined by Gregor (48):

$$K_s^w = \left(\frac{n_w}{n_s}\right)_r \left(\frac{n_s}{n_w}\right)$$

where n_w represents the number of moles of water in the system, n_s is equal to the number of moles of solvent, and r signifies the resin phase. Generally, resins appear to prefer the most polar solvent (usually water) and the preference is highest when the content of the polar solvent in the system is very low. The degree of swelling of the resin apparently is an important consideration and is closely related to the preferential sorption of polar solvents from a mixed system. In summarizing and clarifying the previous researches Helfferich (4) has utilized the selective absorption of solvents by resins to explain the sorption equilibrium of a metal as a distribution of the solute between two liquid phases, namely between the liquid in the resin and that in the external liquid phase. The resin thereby acts as a solid support for the pore liquid while it is simultaneously responsible for the difference in composition of the two liquid phases. It is concluded that the distribution of the dissolved electrolyte depends on differences in dissociation and solvation of the electrolyte in the two phases in addition to the interactions with other constituents of the resin.

Yoshino and Kurimura (15), in their studies of the effect of organic solvents to increase the absorption of metal anionic complexes, found that the addition of organic solvents favors the dehydration of aquated metal ions thereby favoring the stepwise formation of negatively-charged anionic complexes. For zinc(II) in an alcoholic hydrochloric acid system they proposed the following equilibria:

$$Zn(H_2O)_4^{++} + Cl^- \rightleftharpoons ZnCl(H_2O)_3^+ + H_2O \qquad (1)$$

$$ZnCl(H_2O)_3^+ + Cl^- \rightleftharpoons ZnCl_2(H_2O)_2 + H_2O \qquad (2)$$

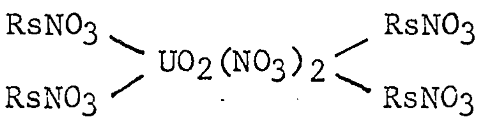
$$ZnCl_2(H_2O)_2 + Cl^- \rightleftharpoons ZnCl_3(H_2O)^- + H_2O \qquad (3)$$

$$ZnCl_3(H_2O)^- + Cl^- \rightleftharpoons ZnCl_4^= + H_2O \qquad (4)$$

These results were verified by a straight-line relationship between the logarithm of the distribution coefficient and the weight percent concentration of organic solvent (in the range of 0 to 60% organic) in the mixed system. From this the enhanced stability of the chloride complexes of all cations, and particularly those cations which are only weakly taken up from aqueous solution by anion exchange resins is readily explained.

Korkisch and co-workers have, in the course of their investigations, discussed several theoretical aspects of the effects of nonaqueous solvents in anion exchange chromatography (9,23,27,30,32,34,44). In their studies of uranium(VI) in chloride systems they found that the adsorption of uranium as a chloride complex from solutions containing aliphatic alcohols and hydrochloric acid increases with increasing concentrations of alcohol, with the chain length of the alcohol, with decreasing dielectric constant of the solvent medium, and with increasing acid concentration in the system. They illustrated the effect of dielectric constant of the system by relating the extraction data for uranium at 99% alcohol, 1% 6M hydrochloric acid in varying alcohols, where the distribution coefficient ranged from zero in aqueous systems (dielectric constant of 88.0) to 1.0×10^5 in dioxane (dielectric constant of 3.0) (23). They assume that the dissociation of UO_2Cl_2 is repressed in low dielectric media and that the undissociated molecules are directly adsorbed by the chloride form of the resin to produce a structure such as

$(RsCl)_2(UO_2Cl_2)$. This is supported by the fact that in the absence of added hydrochloric acid, uranium(VI) is adsorbed from aqueous methyl alcohol where no possibility of the formation of charged complexes prior to adsorption exists. In the case of the nitrate system they have postulated (30) that the adsorbed form of the uranium has the structure:



$$\left.\begin{matrix}\mathrm{RsNO_3}\\\mathrm{RsNO_3}\end{matrix}\right\rangle \mathrm{UO_2(NO_3)_2} \left\langle\begin{matrix}\mathrm{RsNO_3}\\\mathrm{RsNO_3}\end{matrix}\right.$$

They report further that in simple alcohol-hydrochloric acid-water systems with dielectric constants in the range of 18-31.2, the logarithm of the distribution coefficient is approximately proportional to the reciprocal of the dielectric constant of the solvent mixture employed (27). The sole dependence on dielectric constant changes to explain distribution data is not generally applicable however, and is valid only upon comparison of systems containing the same mineral acid in identical concentrations and in which the only variation is in alcohols of very similar structures.

Korkisch (34) also observed the effect of the ionic radius of the metal on its distribution coefficients in a mixed solvent system. His studies indicate that the increase in adsorption of a solute with the addition of an organic is more dramatic for metals with larger ionic radii than for those with smaller ionic radii. He showed furthermore that the effect is most pronounced in the case of the transition elements.

Marple (37) studied the adsorption of lead(II) nitrate complexes on anion exchange resin from nitric acid-water-isopropyl alcohol, and found that sorption proceeded through a neutral $Pb(NO_3)_2$ complex. This was reflected in a linear relationship of the logarithm of the distribution coefficient with the mole fraction of isopropyl alcohol and was shown thermodynamically to be due to a linear free energy of solvation change with mole fraction of isopropyl alcohol. He concluded that the mechanism of adsorption involves only the neutral complex and that solvation of the neutral complex in the solution phase is the primary factor affecting the distribution of a species. Similar findings were reported (13) for thorium(IV) and uranium(VI) in alcoholic nitric acid and in alcoholic hydrochloric acid solutions. Marple concluded that the major factor affecting the distribution of these species is the change in free energy of solvation of the neutral complex with the change in alcohol concentration.

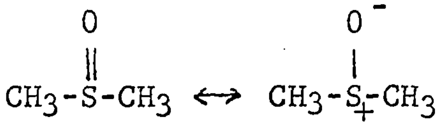
Finally Fritz and Waki (38,39) have demonstrated the multiplicity of species present in mixed solvent systems. They studied first the silver(I) nitrate complexes present in an isopropyl alcohol-water-nitric acid system with both anion and cation exchange resins and then the nitrate complexes of mercury(II), calcium(II), and magnesium(II) in similar systems. In the case of silver they found that while Ag^+ is the predominant species in aqueous solution, $AgNO_3$ exists to the extent of greater than 70% in 90% isopropyl alcohol-0.5$\underline{M}$ nitric acid. At the same time the predominant species in the resin phase are $Ag(NO_3)_3^=$ and $Ag(NO_3)_2^-$.

From the above considerations it appears that no clear-cut correlation has been given for the anion exchange behavior of metals in mixed solvents. Several important effects can be cited but no quantitative treatment exists with regard to the magnitude of any one effect, at least not at the present time. It does seem evident that the presence of an organic solvent enhances the dehydration of metal-aquo complexes and hence the formation of anionic complexes. The sorption of many complexes as neutral molecules or ion pairs, the formation of which is enhanced by a lower dielectric constant solvent system than by water alone, has also been established. Whether these factors combine in an additive manner or interact synergistically to produce an enlarged effect has not yet been determined, and probably will not be until the data from a greater variety of systems can be compared.

Dimethyl Sulfoxide

Dimethyl sulfoxide, the lowest member of the group of sulfoxides with a general formula RSOR, was first prepared in 1866 by Saizew (51,52) using nitric acid to oxidize dimethyl sulfide. Owing to the limited interest shown in the product, no attention was given to its properties and characteristics until many years later. In the late 1940's, an economic process for the production of dimethyl sulfoxide through the oxidation of the waste "black liquor" of sulfite pulp manufacture was developed. Since that time its unique solvating powers have been recognized and a great deal of work has been done to characterize the solvent and to extend its usefulness. Recently several excellent reviews of the chemistry of the sulfoxides in general and of dimethyl sulfoxide in particular have become available. Szmant (53) has reviewed the chemistry of the sulfoxide group with respect to structural aspects, methods of preparation, and chemical behavior of its compounds, and Parker (54) has paid considerable attention to the unusual solvating power of dimethyl sulfoxide in his article dealing with the effects of solvation on the properties of anions in dipolar aprotic solvents. Ranky and Nelson (55) provide an excellent discussion restricted exclusively to the preparation, physical, chemical, and solvent properties of dimethyl sulfoxide. In addition, a general review of the chemistry of this compound is given in two commercial publications of the Crown Zellerbach Corporation (56,57).

Fundamentally dimethyl sulfoxide is a colorless, odorless organic liquid which is highly polar, water miscible, and very hygroscopic. Some of its physical properties have been summarized in Table 1. The electronic structure of the compound may be represented as a resonance hybrid shown below.



$$CH_3-\overset{\overset{O}{\|}}{S}-CH_3 \leftrightarrow CH_3-\overset{\overset{O^-}{|}}{\underset{+}{S}}-CH_3$$

The high degree of polarity in the S-O bond is indicated by the strength of the hydrogen bonds formed between dimethyl sulfoxide and water (58). A considerable reduction in volume is observed on mixing the two liquids, and it is concluded that the hydrogen bonds between dimethyl sulfoxide and water are actually stronger than those in pure water.

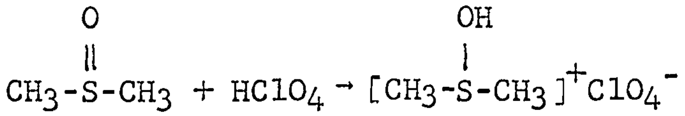
Evidence has been cited to favor a 2:1 association complex between water and dimethyl sulfoxide. Studies have also been made regarding the hydrogen bonding between dimethyl sulfoxide and such solvents as methyl alcohol and chloroform (59).

Table 1. Some physical properties of dimethyl sulfoxide (55, 57)

Molecular weight	78.13
Boiling point at 760 mm Hg	189°C.
Melting point at 760 mm Hg	18.45°C.
Specific gravity at 20°C.	1.1008 gm./ml.
Dielectric constant	48.9 (20°C.)
	45.5 (40°C.)
Dipole moment	3.9 ± 0.1 Debye units

Chemically, dimethyl sulfoxide is generally considered stable, although 70% perchloric acid reacts instantly and explosively on contact with the solvent (55). It can be oxidized to the sulfone with such reagents as potassium permanganate (60), and chromic acid (61), or reduced to the sulfide with zinc and acetic acid (62), hydrogen iodide, or hydrogen sulfide (55). Commercially the preparation of sulfones (and sulfides) from sulfoxides has been carried out catalytically using osmium tetraoxide (63,64) and electrolytically (65), and their reduction to hydrocarbons using pyrophoric nickel catalysts (66).

Although many reactions of dimethyl sulfoxide are well known, its quantitative determination has, for many years, posed some difficulty. The earliest proposed method involved a combustion technique specifically designed for sulfoxides (67), and this was followed by an oxidation-reduction method (68) which is useful but rather complicated to perform. The slight basicity of dimethyl sulfoxide has been taken advantage of in what is perhaps the simplest and most convenient method for its determination. Dimethyl sulfoxide can be quantitatively titrated in acetic anhydride using perchloric acid as a titrant (69,70). The titrations are carried out potentiometrically using either acetic anhydride or dioxane as a solvent for the perchloric acid. The analytical reaction is the following:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3 + HClO_4 \rightarrow [CH_3-\overset{\overset{\displaystyle OH}{|}}{S}-CH_3]^{+}ClO_4^{-}$$

Since neither sulfides nor sulfones have basic properties, they do not interfere in the titration.

Of primary interest is the nature and extent of the unusual solvating powers of dimethyl sulfoxide, especially with respect to inorganic salts. Salts dissolve in a solvent if either the total of anion solvation, cation solvation, and ionizing power of the solvent (expressed by its dielectric constant) or the ion-pair solvation exceeds the crystal energy of the salt (54). The high dielectric constant of dimethyl sulfoxide combined with its tendency to form stable complexes with metals (primarily with the transition metals) may account for some of its great solvating powers.

Cotton and Francis (71) observed the resemblance of the sulfoxides to the phosphine oxides which are known to form coordination compounds with Lewis acids and metal ions. They found the sulfoxides to behave similarly, and report the composition and color of many transition metal halide complexes with dimethyl sulfoxide. From their work it was evident that with the exception of palladium(II) in $PdCl_2 \cdot 2DMSO$ where infra-red evidence suggests a Pd←S coordination, oxygen is the donor atom. Meek and co-workers (72) studied the transition metal ion complexes of dimethyl sulfoxide and found them to have the general formula $(M[DMSO]_n)[MX_4]$ where n is 4 or 6 and X is halogen. Using dimethyl sulfoxide as a solvent and cobalt(II) as a metallic ion they concluded that chloride is more, and iodide less-strongly coordinated than sulfoxide, and that evidence for a complex equilibrium exists.

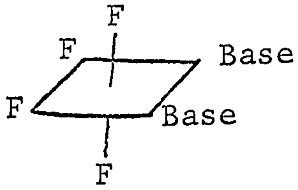
Selbin et al. (73) found that with divalent metals and iron(III), empirical formulas for some metal-dimethyl sulfoxide complexes show 1, 2, or 3 moles of dimethyl sulfoxide per mole of salt suggesting that an anion coordinated in all cases. The aluminum(III) chloride complex with 6 molecules of dimethyl sulfoxide in its structure was the only exception. In their studies they correlated the decrease in strength of the sulfur-oxygen bond in dimethyl sulfoxide with the increase in the strength of the metal-oxygen attraction, and proposed the following stability series:

a) for divalent chlorides: Hg<Ni<Co<Cd<Pb<Cu

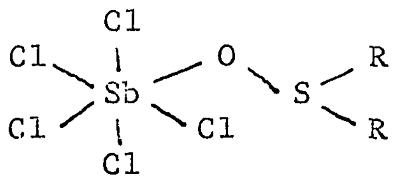
b) for divalent perchlorates: Ni<Mn<Co<Fe<Pb<Cu

c) for trivalent ions: Al<Ga<Fe

The stereochemistry of some metal fluoride-dimethyl sulfoxide complexes was studied by Muetterties (74). He found that for $TiF_4 \cdot 2DMSO$ and analogous compounds with silicon(IV), zirconium(IV), germanium(IV), tin(IV), and molybdenum(IV) the structure was



In the case of the antimony(V) chloride complex, $SbCl_5$·DMSO, Lindquist and Einarsson (75) showed it to have the structure:



The bonding in most of the metal coordination complexes with dimethyl sulfoxide is quite strong, often equivalent in strength to the bonding in the corresponding aquo derivative (56), however in the presence of an excess of water most metal-dimethyl sulfoxide complexes are rapidly hydrolyzed. Strong dimethyl sulfoxide complexes may be formed nevertheless from metal salt hydrates in the presence of large amounts of dimethyl sulfoxide. Several of the metal-dimethyl sulfoxide complexes have been found to be unusually stable: the $SnCl_4$·2DMSO complex can be prepared in aqueous solution, and may be sublimed at 180°C. without decomposition (71) and the TiF_4·2DMSO complex can be recrystallized from water.

Although the great majority of work on dimethyl sulfoxide complexes has involved those of metallic compounds, some investigation has been made of non-metallic complexes as well. For example, Laughlin (76) studied the BF_3·DMSO complex and found that it is hygroscopic but that it can be purified by sublimation. In addition, $DMSO \cdot N_2O_2$ has been studied by Addison and Sheldon (77), and Oda and Takashima (78) studied the reactions of the $POCl_3 \cdot DMSO$ complex with dimethylaniline and anisole.

Although dimethyl sulfoxide has found a great deal of use in organic reactions as a catalyst, reactant, and solvent, few analytical applications of it have been made. Wickberg (79), in his investigation of the paper chromatography of the acetates of sugars, sugar alcohols, cyclitols, and glycosides found dimethyl sulfoxide to be the preferred polar solvent for the work, and Vinson, Fritz, and Kingsbury (80) have used dimethyl sulfoxide as a solvent for the rapid quantitative hydrolysis of esters. With these exceptions however, practically no other instances of the applications of dimethyl sulfoxide to analytical problems are recorded in the literature. Now that its great potentials are being recognized it is hard to believe that dimethyl sulfoxide will continue to go unnoticed for analytical use much longer.

EXPERIMENTAL

Apparatus

Laboratory ware: The ion exchange columns used were 29.5 cm. in length. The lower portion of the column, 15 cm. long with an inside diameter of 1.2 cm., held the resin by means of a plug of glass wool. The top part of the column was 7 cm. long with an inside diameter of 3 cm. The liquid flow through the column was controlled with a one-way teflon stop-cock in the middle of a 7 cm. pyrex tube with a 2 mm. bore. Kimble "Kimex" burettes and Corning "Pyrex" pipettes were used throughout this work.

pH meter: All pH measurements were made on a Beckman Model H-2 pH meter equipped with a Beckman #42363 glass electrode and a Beckman #39170 fiber-type calomel electrode.

Spectrophotometer: A Bausch and Lomb Spectronic 600 spectrophotometer was used for all spectrophotometric measurements. One centimeter matched pyrex cuvettes were used as sample containers.

Atomic absorption spectrophotometer: A Perkin Elmer Atomic Absorption Spectrophotometer Model 303 was used with Perkin Elmer hollow cathode lamps for all atomic absorption determinations.

Flame emission spectroscopic apparatus: The burner is described by D'Silva, Kniseley, and Fassel (81) and the experimental readout is described by Golightly (82).

Radiochemical apparatus: A Nuclear Chicago Anti-Walk Single Channel Analyzer Model 27352 spectrometer was used to isolate gamma emission from the tracers used. A Nuclear Chicago Decade Scaler Model 27104 counted the pulses received from the spectrometer, and the detector used was a 3x3 inch NaI(Tl) scintillation type crystal from the Harshaw Chemical Company.

Stirrer: A Burrell shaker was used in the equilibration of samples for distribution studies.

Reagents

Ion exchange resin: Amberlyst XN-1001 macroreticular anion exchange resin (Rohm and Haas Company, current designation Amberlyst A-26) was used throughout this study. The active sites for anion exchange in this resin and in all other strongly basic anion exchange resins are quaternary ammonium groups. It was ground in a Waring blender and sieved to 60-100 mesh before use. The anion exchange resin was regenerated as follows: About 150 gms. of the resin in a large diameter column (8.5 cm.) was first back-washed with distilled water to remove any fine particles. The resin was then washed with two liters of 2.5M perchloric acid to remove metal ions, after which it was rinsed with water and converted to the chloride form by washing successively with two liters of 2.5M hydrochloric acid and with two liters of 1.0M hydrochloric acid. The resin was rinsed with water, then with absolute ethyl alcohol and finally with acetone after which it was air-dried on filter paper for 24 hours. For column experiments the air-dried resin was soaked in the eluting solution prior to its addition to the column. It was added to the column in the eluting solution and washed with about 30 ml. of this solution prior to the addition of metal samples.

EDTA [disodium dihydrogen(ethylenedinitrilo)tetraacetate dihydrate]: The EDTA was white label grade obtained from the Eastman Chemical Company.

Organic solvents: J. T. Baker purified methyl alcohol, absolute ethyl alcohol, and acetone, and Matheson Coleman and Bell white label methyl sulfoxide (anhydrous) were used throughout this work.

Organic solvent-hydrochloric acid mixtures: The mixtures were made by adding concentrated hydrochloric acid to the appropriate amounts of organic solvents. The mixtures were expressed as percent of one organic constituent in terms of the total volume of the organic solvents, and molarity (M) of the hydrochloric acid.

Metal ions investigated: All metals used for this investigation except molybdenum(VI), zirconium(IV), silver(I), indium(III), uranium(VI), thorium(IV), and vanadium(IV) were reagent grade chloride salts. Molybdenum was used as ammonium molybdate; uranium, silver, and thorium as the nitrates; vanadium as the sulfate ($VOSO_4$); and indium as the chloride prepared from metallic indium. Zirconium was obtained as hafnium-free zirconyl chloride ($ZrOCl_2$) from the Ames Laboratory of the U. S. Atomic Energy Commission.

Radioactive metal sample: Radioactive silver(I) ($Ag^{110m-110}$-260-day half-life) was obtained from Oak Ridge National Laboratory in the form of silver(I) nitrate in 3M nitric acid.

Metal ion solutions: Solutions for distribution coefficients were prepared with metal concentrations of 0.05M by dissolving the metal salts in either dimethyl sulfoxide or methyl alcohol, and adding sufficient hydrochloric acid to effect solution only when necessary. Metal solutions used for most column separations were prepared by dissolving the metal salts in 50% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid so that the metal ion concentration was 0.01M.

Indicator solutions: Eriochrome Black T (Harleco-Hartman-Heddon Co. #883) was used as a solution made by dissolving 0.20 gm. of the solid indicator in 15 ml. of triethanolamine and 5 ml. of absolute ethyl alcohol to reduce its viscosity (83). Metalphthalein (o-cresol phthalein) indicator (LaMont Laboratories, Dallas, Texas) solution was made up in aqueous ammonium hydroxide containing 50% ethyl alcohol (84). Naphthyl Azoxine S (NAS, 8-hydroxy-7-(6-sulfo-2-naphthylazo)-5-quinolinesulfonic acid disodium salt) was obtained from the Eastman Chemical Company and was used as a 0.5% (by weight) aqueous solution. Xylenol Orange (3,3'-bis(N,N'-di(carboxymethyl)-aminomethyl)-o-cresol sulphonephthalein), obtained from the LaMont Laboratories was used as a 0.5% aqueous solution. Thiomichler's Ketone (4,4'-bix(dimethylamine)thiobenzophenone) obtained from the Eastman Chemical Company was used as an 0.5% solution in acetone. 7,8-Benzoflavone was used as a reversible oxidation-reduction indicator as a solution containing 0.5 gm. of the pure solid reagent in 100 ml. of ethyl alcohol (83).

Metal sample mixtures: Metal sample mixtures were made up from high purity metals obtained from the Ames Laboratory of the U. S. Atomic Energy Commission.

All other chemicals were common reagent grade chemicals. In addition, distilled water was used exclusively throughout this work.

Analytical Procedures

Titration methods

EDTA: Solutions of EDTA were standardized against standard zinc(II) using Naphthyl Azoxine S (NAS) indicator as described by Fritz *et al*. (85). Standard zinc(II) was prepared by weighing an appropriate amount of pure zinc metal, dissolving it in nitric acid, and diluting with water.

Magnesium(II): Magnesium was analyzed by a direct titration with EDTA using Eriochrome Black T indicator as described by Bernard, Broad, and Flaschka (86).

Calcium(II): Calcium was determined by back-titration with magnesium using Eriochrome Black T indicator as described by Bernard *et al*. (86).

Strontium(II): Strontium was analyzed by titration with

EDTA using Metalphthalein indicator as described by Bernard *et al*. (86).

Copper(II), zinc(II), and cobalt(II): These elements were determined by direct titration with EDTA using NAS indicator according to the method of Fritz *et al*. (85). Pyridine was used as the buffer in all cases.

Aluminum(III), indium(III), iron(III), cadmium(II), lead(II), nickel(II), titanium(IV), and vanadium(IV): These elements were determined by back-titration with standard copper(II) at pH 5.5-6.0 after the addition of excess EDTA using NAS indicator. Pyridine was used as the buffer. In the case of titanium, 5 drops of 30% hydrogen peroxide were added prior to the addition of EDTA.

Manganese(II): Manganese was determined by direct titration with EDTA at pH 8.5 using NAS as the indicator. Ascorbic acid was added to the samples prior to titration.

Thorium(IV): Thorium was determined by direct titration with EDTA at pH 2 using Xylenol Orange indicator.

Bismuth(III): Bismuth was determined (87) by back-titration with standard copper(II) at pH 5.5-6.0 after the addition of 1 gm. of sodium chloride, 5 ml. of concentrated hydrochloric acid, and an excess of EDTA. Pyridine was used as the buffer, and NAS as the indicator for the titration.

Tin(IV): Tin was analyzed (88) by boiling the samples 5 minutes after the addition of 1 gm. of sodium chloride, 5 ml. of concentrated hydrochloric acid, 1 ml. of concentrated sulfuric acid (to prevent volatilization of tin(IV) chloride) and an excess of EDTA. The solutions were cooled and the excess EDTA back-titrated with standard copper(II) using NAS indicator. Pyridine was used as a buffer.

Zirconium(IV): Zirconium was analyzed by back-titration with standard thorium(IV) at pH 2 after the addition of excess EDTA. Xylenol Orange was used as the indicator.

Mercury(II): Mercury was determined (89) by direct titration with EDTA at pH 6 using Thiomichler's Ketone as an indicator. Pyridine was used as a buffer.

Arsenic(III) and antimony(III): These elements were determined by oxidation-reduction titration with potassium bromate according to the method of Vogel (83) after the solutions were neutralized and boiled to remove the organic solvent. The indicator used was 7,8-benzoflavone.

Colorimetric method

Uranium(VI): Uranium was determined colorimetrically in 30% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid as its yellow complex with dimethyl sulfoxide. Readings were taken at 428 mμ.

Flame emission spectroscopic method

Silver(I) and molybdenum(VI): Silver and molybdenum were determined by flame emission spectroscopy. All samples were submitted to Analytical Services Group II of the Ames Laboratory for analysis. Silver was determined in solutions of 30% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid using an oxy-hydrogen flame. The emission line used for analysis was 3386Å. Molybdenum was determined in solutions of 30% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid using a fuel-rich oxy-acetylene flame. The analysis line was 3978Å.

Atomic absorption spectroscopic method

Gold(III): Gold was analyzed by atomic absorption spectroscopy. Samples in 30% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid were submitted to Analytical Services Group I of the Ames Laboratory for analysis. A gold hollow cathode lamp was used and absorption measured at a wavelength of 2428Å.

Radiochemical method

Silver(I): Silver$^{110m-110}$ (260-day half-life) was used in a column study to demonstrate its quantitative elution with concentrated hydrochloric acid. It was added as a tracer in a stock solution of silver chloride and after elution its recovery was determined by comparison of the counts of the recovered sample with those in an identical aliquot taken from the stock solution. The instrument was set at a threshold energy of 0.600 Mev. and a window width of 0.400 Mev. was used. The total activity added to the column was 0.25 μc. and 2% of this was counted for recovery evaluation.

Measurement of Distribution Coefficients

A study of the behavior of metal ions on ion exchange resin under given conditions can effectively be approached from one of two directions. On one hand it is possible to determine batch distribution coefficients of metals and relate these values to column behavior, or alternatively column elution experiments can be run which are then qualitatively described by distribution coefficients calculated from the observed elution curves. The former method is the most efficient for it permits a more rapid and systematic study of variables such as acid concentration and solvent choice, and does not require laborious plotting of elution curves otherwise necessary.

Distribution coefficients are a convenient means of describing the extent to which a metal is taken up from a solution by an ion exchange resin and they may be expressed in a variety of units. The most convenient definition for this work was in terms of the amount of metal per gram of dry resin and the amount of metal per milliliter of solution found after equilibration. The batch distribution coefficient, D, may therefore be computed according to Equation 1:

$$D = \frac{\text{mmoles. of metal on the resin/gram of dry resin}}{\text{mmoles. of metal in solution/ml. of solution}} \quad . \qquad (1)$$

The batch distribution coefficient obtained from equilibration studies may be related to the volume distribution coefficient, D_V (obtained from column elution studies) by Equation 2 where ρ is the bed density (grams of dry resin per

$$D_V = \rho D \qquad (2)$$

milliliter of resin bed). A value for ρ can be determined by measuring the volume of a settled wet column of resin whose dry weight was known exactly. It is possible to relate D_V to the volume of eluent required to elute a given constituent to its elution maximum on the Gaussian elution curve by the following equation (Equation 3):

$$V = Ad(D_V+i) \quad . \qquad (3)$$

where V is the volume of eluent in ml. which moves a band maximum d (in cm.) in a column of cross-sectional area A (sq. cm.) and a fractional interstitial volume i. From this equation it is possible to get a good estimate of the volume of eluent needed to elute a substance from any particular size column.

In terms of metal ion separations it is useful to compare the preference of an ion exchanger under a particular set of conditions for one metal (A) over a second metal (B). For this purpose the separation factor, α_B^A is the quantity utilized. The separation factor is defined by Equation 4 below and as a general rule this value should be greater than ten for optimum separations.

$$\alpha_B^A = \frac{D_A}{D_B} \qquad (4)$$

Distribution coefficients were determined in the following manner: quantities of approximately one gram of air-dried anion exchange resin were accurately weighed into 250-ml. ground-glass stoppered erlenmeyer flasks. Fifty milliliters of the appropriate solvent mixtures containing 0.20 mmole. of the metal ion of concern were then pipetted into the flasks. The flasks were tightly stoppered and shaken on a Burrell shaker until equilibrium was attained. Three 10-ml. aliquots were taken of the liquid phase which had been filtered free of resin, and these were analyzed for the metal ion present. Distribution coefficients were calculated in terms of the weight of the air-dried resin and then corrected once the weight-loss of the air-dried resin on heating at 110°C. for two hours had been determined. The resin was found, generally, to lose 9% of its weight on drying.

In order to determine the time period required for equilibration of a metal solution with the resin phase, a kinetic study was made using copper(II) as a representative element. Distribution coefficients of copper(II) in 20% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid were determined as a function of equilibration time. From this study an equilibration time of 2 hours was chosen for all distribution studies.

Column Separation Procedure

In preparing an ion exchange column the air-dried resin was first slurried in a beaker with the solvent mixture being used. This was then added to a glass column to the desired height. A glass wool plug was used to contain the resin in the column. For most separations a column height of 8 cm.

was used. About 30 ml. of the solvent mixture were then passed through the column at a moderate flow rate to insure the attainment of equilibrium and also to help settle the resin. A glass wool plug was placed at the top of the resin bed to help stabilize the resin when samples and eluents were added. The metal ion sample mixture was prepared by pipetting 5 ml. of each metal (each dissolved in the first eluting solvent) onto the column. This was sorbed into the resin at a flow rate of 1 ml./min. and the first component eluted, usually by passing an additional 15 ml. of the eluting solvent through the column at the same flow rate of 1 ml./min. Following the eluting of the first metal the eluent was changed to elute the second component. It was never necessary to reduce the flow rate below 1 ml./min. to effect any of the separations performed. Metal recoveries were determined by titrimetric or by other means.

Sampling Technique

Three sampling techniques were employed in the separation studies. The first involved the pipetting of 0.01M solutions of metal salts dissolved in 50% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid. This method was used to test the quality of separations predicted on the basis of distribution coefficients. Once separation schemes had been demonstrated sample mixtures were made up from high purity metals obtained from the Ames Laboratory of the U. S. Atomic Energy Commission. These were accurately weighed out into 50-ml. beakers, covered, and dissolved in concentrated hydrochloric and nitric acids over low heat. The total volume of the samples was reduced to between 5 and 10 ml. and one of two procedures was then used to transfer the samples. In some cases samples were rinsed directly onto the previously prepared column with 50% dimethyl sulfoxide-methyl alcohol and the entire sample separated and analyzed. The major limitation of this technique was found to be the small quantities of metal that had necessarily to be weighed out to eliminate exceeding the capacity of the column. To aleviate this problem a third technique was used: larger metal samples were accurately weighed out and dissolved in a mixture of concentrated nitric and hydrochloric acids over low heat. Again the volume was reduced to about 10 ml. and the sample was transferred to a 100-ml. volumetric flask with 50% dimethyl sulfoxide-methyl alcohol. The sample solution was then well mixed and 5-ml. aliquots were taken for separation and analysis.

DISCUSSION OF DISTRIBUTION COEFFICIENT DATA

Choice of Systems

Previous studies of the effects of organic solvents on the anion exchange behavior of metals (27) indicate that the greatest degree of differentiation between elements highly sorbed and those not at all sorbed by an anion exchange resin at low acid concentrations occurs when methyl alcohol is used as the organic solvent. Similar results were also observed in acetone; however, in the latter case very few metals were only slightly sorbed while the majority were taken up strongly. In a methyl alcohol medium approximately one-half of the elements studied showed strong sorption while the other half showed virtually no sorption at all. For this reason, methyl alcohol was chosen as the solvent to be used in conjunction with dimethyl sulfoxide for these studies. An additional feature of methyl alcohol which makes it especially useful in combination with dimethyl sulfoxide is that many metal salts have a high degree of solubility in methyl alcohol, thus eliminating the solubility problems at low concentrations of dimethyl sulfoxide which might otherwise be encountered.

The choice of 0.6M hydrochloric acid for use throughout the largest part of this study was made primarily so that correlations could be drawn between this work and data reported in the literature. Marple's studies of the sorption mechanism of lead(II) (37), uranium(VI), and thorium(IV) (13) onto anion exchange resins from nonaqueous solution were carried out in 0.3M and 0.5M acid solutions, while the sorption studies of Fritz and Waki (38,39) were carried out in 0.5M acid solutions. In addition, the work of Korkisch (27) involving the anion exchange behavior of metals in nonaqueous systems was performed in solvent systems containing 0.6M acid. Thus the choice of 0.6M hydrochloric acid appeared reasonable not only so that data could be interpreted from a mechanistic standpoint but also so that comparisons could be made with distribution behavior reported by other workers.

The characteristics of the ion exchange resin used throughout this study are worthy of special comment. Most conventional anion exchange resins (e.g. Dowex 1) are polymers formed in the emulsion copolymerization of styrene with divinylbenzene. The resulting spherical beads are then treated to introduce a basic functional group, for example the quaternary ammonium group. The product is a flexible carbon-hydrogen structure containing basic active sites suitable for anion exchange and permeated by a network of tiny pores through which liquids can flow. Because of the minute size of the pores in the beads, organic molecules pass through only with difficulty. These resins have gel-like properties in solution and one result of this is a measurable shrinking and swelling of the resin if the nature of the solvent is altered. These size changes, coupled with the extremely long equilibration time required for metals when studied in nonaqueous solvents pose difficulties in their ease of analytical application.

A second process has been developed for the production of anion exchange resins and the product is much better suited for studies in nonaqueous solvents. If a properly selected organic solvent is added to the copolymerization mixture of styrene and divinylbenzene the resultant polymer beads are characterized by the extremely large pores (several hundred angstroms) which permeate the spherical beads (90). This pore system is retained by the beads in the dry state as well as when they are mixed with a solvent. These resins are termed "macroreticular" and are unique in that their large pore system permits a large contact surface between the resin and solution which is accessible to aqueous and organic solvents with equal ease. The macroreticular resins do not swell and shrink as solvent properties are changed and because of the large contact surface and large pores, equilibrium is reached much more rapidly than with conventional resins.

Amberlyst XN-1001 anion exchange resin, used for this work, is a macroreticular resin. Its rapid equilibration time with metals in nonaqueous solvent mixtures makes it well-suited for batch distribution studies. A comparison of equilibration times for copper(II) with Amberlyst XN-1001 and with Dowex 1x8 in the dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid system is shown in Figure 1. In addition, the failure of the resin to shrink and swell in solvent mixtures of varied compositions makes it ideal for column experiments.

Discussion of Distribution Coefficients

Distribution coefficients for 26 elements were measured in a dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid mixed solvent system where the proportions of dimethyl sulfoxide and methyl alcohol present were varied. These data are presented in Table 2. It is notable that with the exceptions of nickel(II), titanium(IV), calcium(II), magnesium(II), strontium(II), vanadium(IV), molybdenum(VI), thorium(IV), and

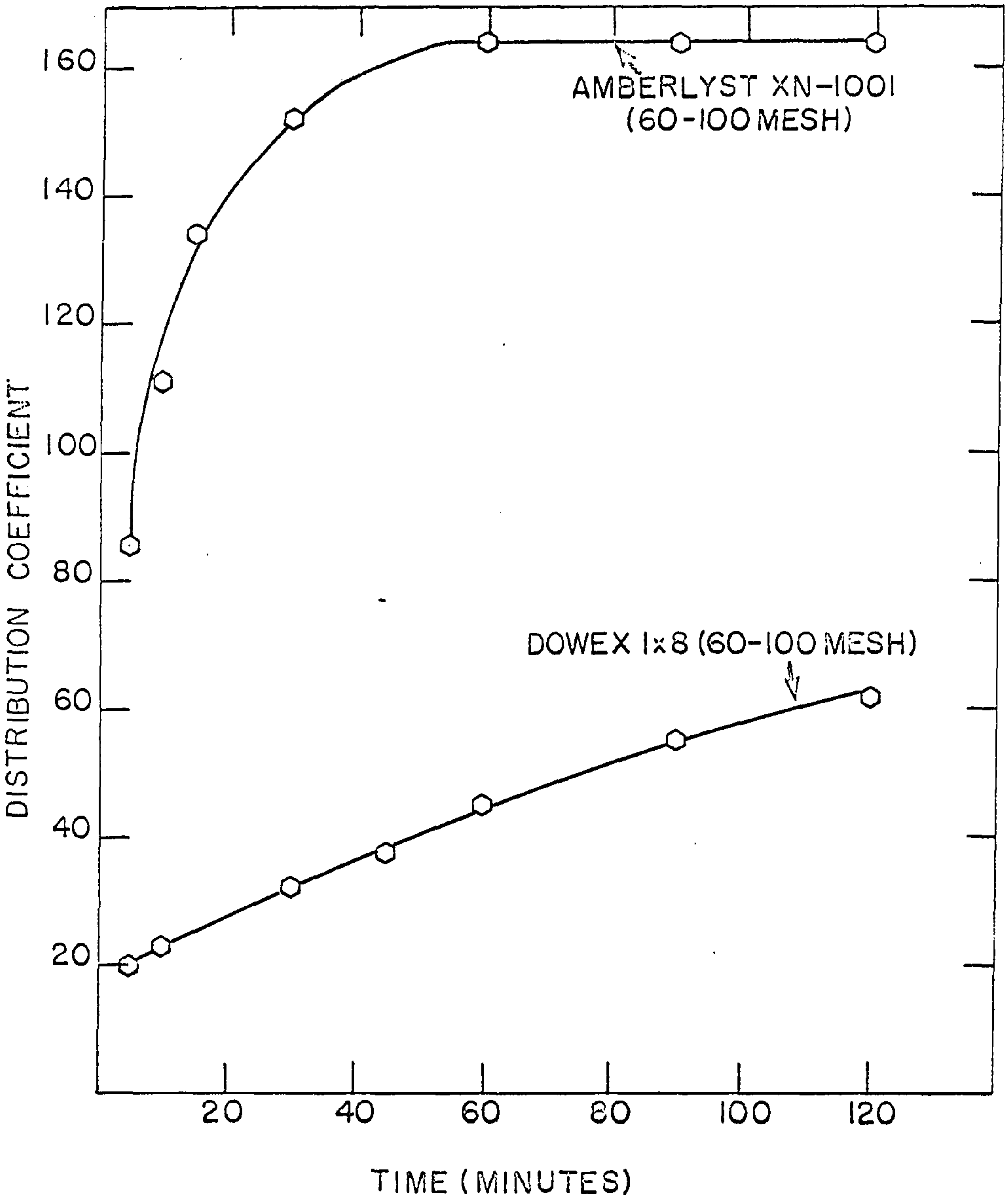


Fig. 1. Comparison of the equilibration rates of copper(II) between Amberlyst XN-1001 and Dowex 1x8 anion exchange resins from 30% DMSO-MeOH-0.6M HCl

Table 2. Distribution coefficients of metal ions on Amberlyst XN-1001 resin from dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid solutions

% DMSO	DMSO	Ca(II)	Mg(II)	Sr(II)	Ti(IV)	Zr(IV)	VO^{+2}	Mo(VI)	Mn(II)	Fe(III)
0%									65	147
1%	0.005									121
2%	0.010									107
5%	0.026								48	52
7%	0.037									36
10%	0.054								38	20
12%	0.065									14
15%	0.082								29	8.8
20%	0.111					0.24			24	4.8
30%	0.175	$\sim$0	$\sim$0	$\sim$0	0.03	0.12	$\sim$0	$\sim$0	16	1.0
40%	0.243					0.12				0.14
50%	0.319	$\sim$0	$\sim$0	$\sim$0	0.16	0.12	$\sim$0	$\sim$0	12	$\sim$0
60%	0.402	$\sim$0	$\sim$0	$\sim$0	0.26		$\sim$0	$\sim$0		$\sim$0
80%	0.598	<1	<1	<1	0.41		$\sim$0	$\sim$0		$\sim$0
100%	0.844									$\sim$0

Table 2. (Continued)

% DMSO	DMSO	Co(II)	Ni(II)	Cu(II)	Ag(I)	Au(III)	Zn(II)	Cd(II)	Hg(II)	Al(III)
0%						380				
1%	0.005					352				
2%	0.010									
5%	0.026					233				
7%	0.037									
10%	0.054					143				
12%	0.065									
15%	0.082					89				
20%	0.111	273		239		68		1004		
30%	0.175		0.48	168		35	626		2885	~0
40%	0.243			122				444		
50%	0.319	132	0.83	87	85	11	213	298	551	~0
60%	0.402	100	0.94	69	47	5.7	125	179	281	~0
80%	0.598	57	1.2	44	16	1.4	50	71	87	
100%	0.844			29	3.1			33		

Table 2. (Continued)

% DMSO	DMSO	In(III)	Sn(IV)	Pb(II)	As(III)	Sb(III)	Bi(III)	Th(IV)	UO_2^{+2}
0%		292			0.46	339			470
1%	0.005								362
2%	0.010								
5%	0.026	128							153
7%	0.037								
10%	0.054	72							74
12%	0.065								
15%	0.082	43							23
20%	0.111	29		632					8.0
30%	0.175	14	33				8669	~0	~0
40%	0.243								
50%	0.319	4.2	9.7	69			1285	~0	~0
60%	0.402	2.5	7.4				539	~0	~0
80%	0.598	1.7	4.3				107	~0	~0
100%	0.844			11					

aluminum(III), the distribution coefficients for a particular element show a distinct tendency to decrease with increasing proportions of dimethyl sulfoxide.

Graphical analysis of these data is best done using two different types of plots. A plot of the logarithm of the distribution coefficients for metals in solvent systems containing between 0 and 10 to 20% dimethyl sulfoxide against the mole fraction of dimethyl sulfoxide in the system is, for the 5 metals determined, distinctly linear. There is, in all cases, a break in the linearity of the curves in the region of 10 to 20% dimethyl sulfoxide after which point the data are no longer best fit by a straight line. If the logarithms of the remainder of the distribution coefficients (those between 20 and 100% dimethyl sulfoxide) are plotted against the logarithm of the mole fraction of dimethyl sulfoxide in solution then the points are well-fit by a straight line. These graphical representations of the data are shown in Figures 2 and 3.

Although any explanation of these data must necessarily be of a somewhat theoretical nature owing to the lack of understanding of systems as complex as this, several features are clear. First, no detailed information is available to

Fig. 2. Distribution coefficients of five metal chlorides as a function of the mole fraction of dimethyl sulfoxide in a system of dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid

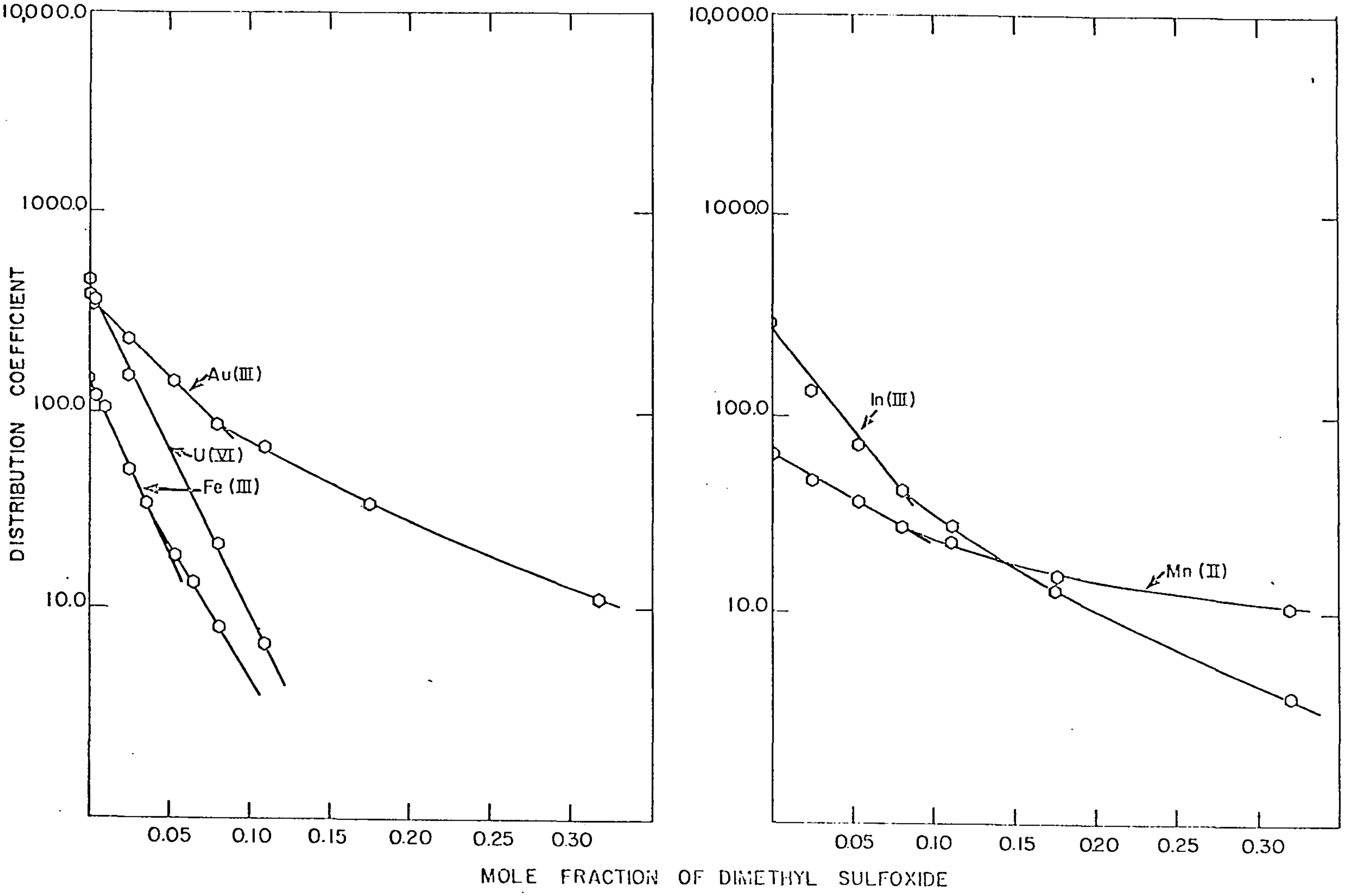
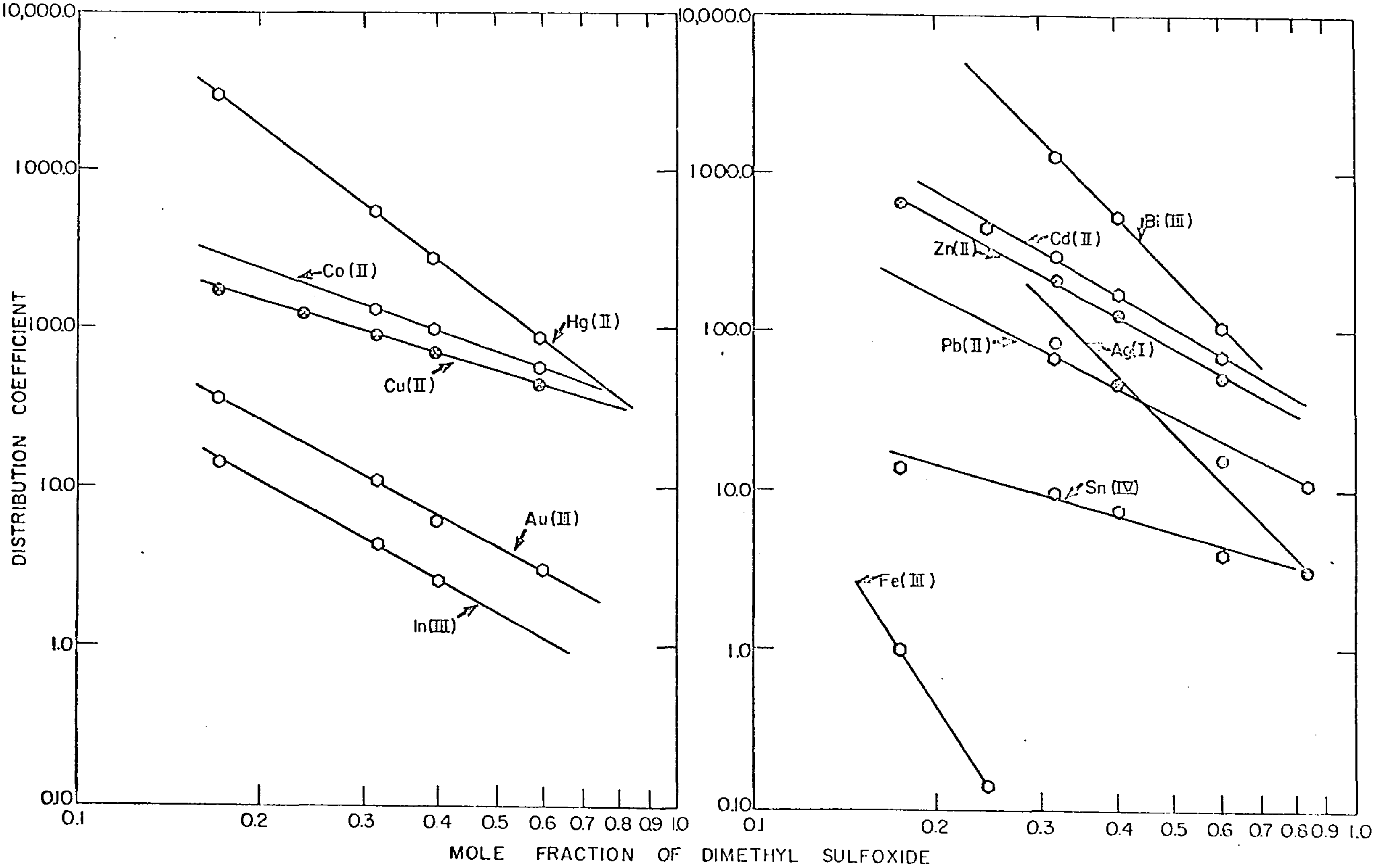

10,000.0
1000.0
100.0
10.0
DISTRIBUTION COEFFICIENT
Au(III)
U(VI)
Fe (III)
0.05
0.10
0.15
0.20
0.25
0.30
10,000.0
1000.0
100.0
10.0
In(III)
Mn (II)
0.05
0.10
0.15
0.20
0.25
0.30
MOLE FRACTION OF DIMETHYL SULFOXIDE

Fig. 3. Distribution coefficients of metal chlorides as a function of the logarithm of the mole fraction of dimethyl sulfoxide in a system of dimethyl sulfoxide-methyl alcohol-0.6_M_ hydrochloric acid


DISTRIBUTION COEFFICIENT
10,000.0
1000.0
100.0
10.0
1.0
0.10
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
MOLE FRACTION OF DIMETHYL SULFOXIDE
Hg(II)
Co(II)
Cu(II)
Au(III)
In(III)
Bi(III)
Cd(II)
Zn(II)
Pb(II)
Ag(I)
Sn(IV)
Fe(III)

describe the precise composition of the resin and solution phases of an ion exchange system such as the one being studied. Evidence has been cited to substantiate the preference of a resin for the most polar solvent in a system. In this work it was found that the resin effectively removes from the solution phase the small amount of water added with the addition of concentrated hydrochloric acid. This water is not, however, enough to saturate the resin phase, and invasion studies would be required before the exact composition of the two phases could be determined.

A second point is clear, however, and that is the marked increase in the distribution coefficients of many metals in a system of methyl alcohol-0.6M hydrochloric acid as contrasted to their values in an aqueous system containing 0.6M hydrochloric acid. This difference may be attributed (15) to the facilitation of the dehydration of the metal-aquo complexes in nonaqueous solvents to form metal-chloro complexes available for sorption. The dehydration equilibria are reviewed below.

$$M(H_2O)_4^{++} + Cl^- \rightleftharpoons MCl(H_2O)_3^+ + H_2O \quad (1)$$

$$MCl(H_2O)_3^+ + Cl^- \rightleftharpoons MCl_2(H_2O)_2 + H_2O \quad (2)$$

$$MCl_2(H_2O)_2 + Cl^- \rightleftharpoons MCl_3(H_2O)^- + H_2O \quad (3)$$

$$MCl_3(H_2O)^- + Cl^- \rightleftharpoons MCl_4^= + H_2O \qquad (4)$$

From the work of Fritz and Waki (38,39), Marple (13,37), and Korkisch (23,30), it is clear that for some cases at least, in acid concentrations as low as 0.6M the reaction sequence proceeds only as far as step (2) to produce the neutral metal-aquo-chloro complex which has been shown to be the species sorbed onto the resin. The reactions to form complex anionic species must occur within the resin phase or through direct interactions with the active sites of the resin.

Marple observed a decrease in the distribution coefficients of lead(II), uranium(VI), and thorium(IV) as pure alcohol systems containing a low proportion of nitric acid were diluted with water. This decrease he related thermodynamically to a decrease in the free energy of solvation of the neutral complex with changes in the alcohol content of the system. The effect of the decrease in solvation energy is represented by a linear decrease in the logarithm of the distribution coefficient of an element with a decrease in the mole fraction of alcohol present in the solvent system.

A similar linear decrease was observed in the dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid system for solutions containing between zero and 10 to 20% dimethyl sulfoxide (Fig. 2). This would suggest that the addition of small amounts of dimethyl sulfoxide to an alcoholic system causes a decrease in the solvation of the neutral complex, the sorbed species. This may appear surprising since dimethyl sulfoxide has a very high affinity for water and it could reasonably be expected that the addition of dimethyl sulfoxide would aid the dehydration process.

A second reaction sequence may suffice to explain the effect of small amounts of dimethyl sulfoxide in decreasing the distribution coefficients of metals over those in pure methyl alcohol-0.6M hydrochloric acid. The strong competition between water and dimethyl sulfoxide for the coordination sites in a metal complex in a nonaqueous solvent permits the possibility of the following equilibrium with the neutral metal-aquo-chloro complex:

$$MCl_2(H_2O)_2 + DMSO \rightleftharpoons MCl_2(H_2O)(DMSO) + H_2O \qquad (5)$$

$$MCl_2(H_2O)(DMSO) + DMSO \rightleftharpoons MCl_2(DMSO)_2 + H_2O \qquad (6)$$

A complex analogous to $MCl_2(DMSO)_2$ was found by Korpak (91) in his studies of the dioctyl sulfoxide complexes of the uranyl cation in hydrochloric acid. If nonaqueous anion exchange behavior can be explained largely by partitioning effects of the metallic species involved between the resin and solution phases, then the decrease in distribution coefficients observed could be due to the increased solubility of $MCl_2(DMSO)_2$ in the solution phase over its solubility in the resin phase. The resin phase, which contains a considerable amount of water, would logically prefer to dissolve the chloro-aquo species as opposed to the chloro-dimethyl sulfoxide complex and thus the formation of the chloro-dimethyl sulfoxide complex of a metal would effectively decrease its distribution coefficient over that in pure methyl alcohol.

The extent of reactions (5) and (6) could be predicted if the relative solvating abilities of water and dimethyl sulfoxide for a particular metal could be determined. This can be done from physical measurements in the following manner. If the solubility of a metal salt in dimethyl sulfoxide and in water were measured at three or more temperatures (T), a linear plot of the reciprocal of the temperature against the natural logarithm of the mole fraction of the metal dissolved in the solvent (ln X) could be made. From this plot the heat of solvation (ΔH_{solv}) of the metal salt in the solvent could be determined using the following relationship

$$\ln X = \frac{-\Delta H_{solv}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

where R is the gas constant and T_m is the melting point of the salt being considered. Although ΔH_{solv} is a composite of many individual terms, it still reflects the energy required for a solvent to break up the crystal lattice of a salt and solvate the individual ionic species in solution. The smaller this energy is, the more strongly the solvent is said to interact with the solute and thus the greater is the solvation of the solute by the solvent. A comparison of the values determined for ΔH_{solv} in dimethyl sulfoxide and in water would be a measure of the differences in solvating abilities of each solvent for a particular metal salt.

A mechanism such as the one proposed would explain the variation in slopes observed in the linear portions of Figure 2. The extent of reactions (5) and (6) would be largely a function of the degree of dimethyl sulfoxide interaction with the specific metal ion present. Since this would not necessarily be identical for any two metals, the slopes of the lines in Figure 2 could reasonably be expected to differ.

The failure of the distribution data to fit a linear relationship in Figure 2 throughout the entire range of dimethyl sulfoxide concentrations is indicative that a second process is occurring at higher proportions of dimethyl sulfoxide. The logarithm of the distribution coefficients for a particular metal at dimethyl sulfoxide concentrations greater than about 20% were found to linearly related to the logarithm of the mole fraction of dimethyl sulfoxide present in the solutions. Korkisch attributed relations such as these to be due to dielectric constant effects. If this were the case it would be expected that the distribution coefficients for different metals would be similarly affected, and thus the slopes of the log-log plots for different elements might be at least approximately equal. It is clear from Figure 3 that this is not the case. In addition, the differences in slopes cannot obviously be correlated with the ionic radii of the metals involved, with the ionic charge on the metals involved, or with the relative positions of the elements on the periodic table. Thus although the logarithms of the distribution coefficients in Figure 3 do decrease as the dielectric constant of the system is increased (i.e. as methyl alcohol, dielectric constant 32.6, is replaced with dimethyl sulfoxide, dielectric constant 48.9), factors in addition to dielectric constant changes alone must influence the behavior of the metals.

A reasonable explanation of the observed solvent effect on the distribution coefficients results from a natural extension of the equilibrium sequences expressed in reactions (5) and (6). In the presence of considerable amounts of dimethyl sulfoxide, reaction (6) would proceed to completion as the result of mass action effects. The neutral species formed, $MCl_2(DMSO)_2$, in the presence of excess dimethyl sulfoxide, can become involved in the equilibrium shown below.

$$MCl_2(DMSO)_2 + 4DMSO \rightleftharpoons [M(DMSO)_6]^{++}2Cl^- \qquad (7)$$

$$[M(DMSO)_6]^{++}2Cl^- + MCl_2(DMSO)_2 \rightleftharpoons [M(DMSO)_6]^{++}[MCl_4]^{=} + 2DMSO \qquad (8)$$

The product of reaction (8), on the basis of partitioning effects, would reasonably be more soluble in the solution phase containing a large proportion of dimethyl sulfoxide than it would be in the resin phase. This would explain the observed decrease in distribution coefficients of metals upon the addition of larger amounts of dimethyl sulfoxide. Further, the dependence of the equilibrium values in Equations (7) and (8) on the relative affinities of different metals for dimethyl sulfoxide would account for the variation in slope observed in Figure 3. The solvolysis studies previously mentioned would provide a basis for the explanation and prediction of the slopes of these lines.

Regarding the data themselves several points merit comment. The effectiveness of dimethyl sulfoxide as a solvating agent in the mixed solvent system studied is exemplified by the inclusion of distribution coefficients for lead(II) and silver(I) in solutions which were only 0.6M in hydrochloric acid. Normally either of these metals would precipitate out of solution as the chloride salt in solutions containing such a low concentration of chloride. It must be pointed out, however, that although lead is stable in solutions containing as little as 20% dimethyl sulfoxide, a minimum of 50% dimethyl sulfoxide is required to keep silver in solution.

A second observation worthy of mention concerns the low distribution coefficients determined for molybdenum(VI), gold(III), uranium(VI) and iron(III) in solutions containing 50% dimethyl sulfoxide. These values would be expected to be quite high (greater than 50) but evidently the solvating ability of dimethyl sulfoxide has a startling influence on the distribution of these elements. Similar findings have been reported regarding the ability of dioctyl sulfoxide to extract many metal ions from hydrochloric acid solutions

(91-93).

A final point worthy of note is the distribution curve for gold(III) in Figure 3. It is reportedly virtually impossible to remove gold(III) for a conventional anion exchanger in the chloride form in aqueous solution. The elution of gold(III) has been carried out by Burstall *et al*. (14) using an acetone eluent; however, this has some disadvantages because gold(III) shows a tendency to be reduced to the metal on standing in acetone. An eluent of 80 to 100% dimethyl sulfoxide-methyl alcohol-0.6*M* hydrochloric acid has qualitatively been shown to effectively elute gold(III) from an anion exchange column in the chloride form. The stability of gold(III) in dimethyl sulfoxide-methyl alcohol mixtures is apparently much greater than it is in acetone and this is a definite advantage of the dimethyl sulfoxide system.

The Effect of Dielectric Constant Changes on Distribution Coefficients

The effect of dielectric constant changes on the distribution coefficients of a metal in a mixed solvent system containing dimethyl sulfoxide was demonstrated in studies using methyl alcohol, acetone, and tetrahydrofuran with dimethyl sulfoxide in 0.6*M* hydrochloric acid. Copper(II) was chosen as a representative metal and distribution coefficients were run in each of 3 systems: dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid, dimethyl sulfoxide-acetone-0.6M hydrochloric acid, and dimethyl sulfoxide-tetrahydrofuran-0.6M hydrochloric acid where the proportion of dimethyl sulfoxide was varied from 20 to 100%. A similar series of distribution coefficients was determined for copper(II) in dimethyl sulfoxide-water-0.6M hydrochloric acid over the same range of dimethyl sulfoxide concentrations to use as a comparison. Data for these distribution coefficients are presented in Table 3. The data for any one system show a distinctly linear

Table 3. Distribution coefficients of copper(II) onto Amberlyst XN-1001 resins from dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid, dimethyl sulfoxide-acetone-0.6M hydrochloric acid, dimethyl sulfoxide-tetrahydrofuran-0.6M hydrochloric acid, and dimethyl sulfoxide-water-0.6M hydrochloric acid systems

Solvent system	20% DMSO	30% DMSO	40% DMSO	50% DMSO	60% DMSO	80% DMSO	100% DMSO
DMSO-MeOH-0.6M HCl	239	168	122	87	69	44	29
DMSO-acetone 0.6M HCl	81	-	54	46	46	35	29
DMSO-THF-0.6M HCl	-	-	37	34	30	29	25
DMSO-H_2O-0.6M HCl	1.2	-	-	2.2	3.5	8.2	29

relationship when the logarithm of the distribution coefficient is plotted against the logarithm of the mole fraction of dimethyl sulfoxide in the system (see Figure 4). It is notable that in no cases are the slopes of the lines identical. The dielectric constants of the pure nonaqueous solvents used for these determinations are tabulated in Table 4 below.

Table 4. Dielectric constants of various organic solvents

Solvent	Dielectric constant
Methyl alcohol	32.6 (94)
Acetone	20.7 (94)
Tetrahydrofuran	8.0 (27)
Dimethyl sulfoxide	48.9 (54)

Korkisch has reported that the logarithm of the distribution coefficient of an element in several simple and closely related nonaqueous systems is inversely proportional to the dielectric constant of the system. That is, if the distribution coefficients for an element in two closely related systems were to be compared, the system in which the distribution coefficient was higher would be the one with the lower dielectric constant. It is not evident from the data presented here that the relationship proposed by Korkisch is

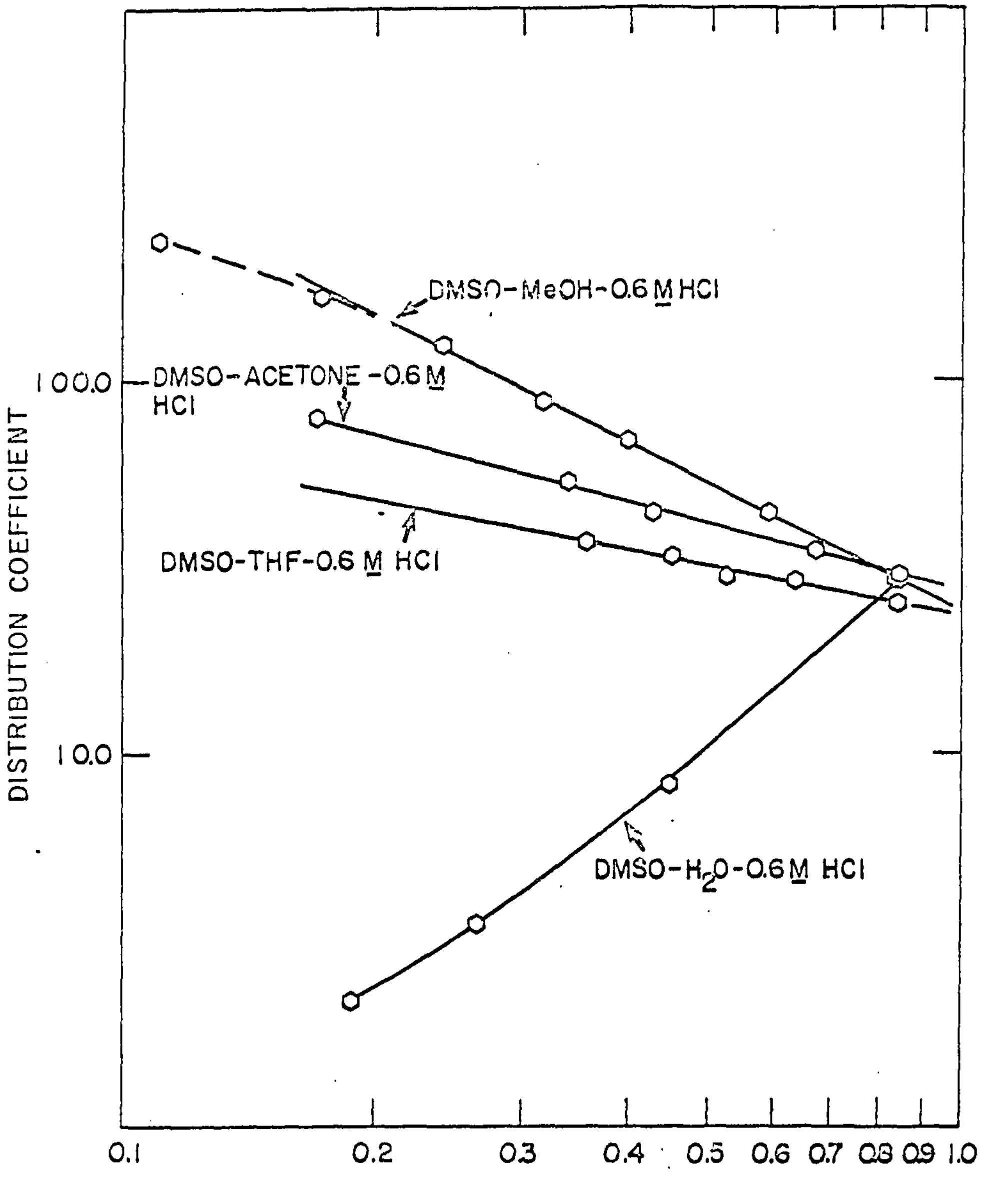


Fig. 4. Distribution coefficients of copper(II) as a function of the mole fraction of dimethyl sulfoxide in various mixed solvent systems on Amberlyst XN-1001 resin

valid for the dimethyl sulfoxide system. A slightly different analysis of the data, however, provides an interesting result.

It would be very difficult to calculate the dielectric constant of systems such as these (i.e. the dimethyl sulfoxide mixed solvent systems), however if only the change in dielectric constant between the two organic solvents used is considered (neglecting the effect of added hydrochloric acid) there appears to be a definite relationship between the slope of the lines in Figure 4 and the reciprocal of the change in dielectric constant in the system. Data have been accumulated in Table 5 to substantiate this.

Table 5. Influences of dielectric constant changes on the slopes of curves expressing the relation of the distribution coefficient of copper(II) to the mole fraction of dimethyl sulfoxide in mixed solvent systems

Mixed solvent	Dielectric constant range Organic	Dielectric constant range DMSO	ΔDC	Slope of curve in Fig. 4	(Slope)x (ΔDC)=K
DMSO-MeOH-0.6M HCl	32.6	48.9	16.3	-0.506	K= -8.25
DMSO-Acetone 0.6M HCl	20.7	48.9	28.2	-0.294	K= -8.29
DMSO-THF 0.6M HCl	8.0	48.9	40.9	-0.200	K= -8.20
DMSO-H_2O-0.6M HCl	78.5	48.9	-29.6	+0.765	K=-22.7

From these data it is clear that in the case of mixed nonaqueous anion exchange systems there is an inverse relationship between the slope of the curves in Figure 4 and the limits in the overall change in dielectric constants of the system. No correlation was found for the data in the dimethyl sulfoxide-water-0.6M hydrochloric acid system as would be expected since the sorption processes are not comparable in the aqueous and nonaqueous systems and thus the effect of dielectric constant changes cannot be expected to be the same.

Acid Concentration Effects on the Behavior of Selected Metals

In order to examine the usefulness of the dimethyl sulfoxide-methyl alcohol-hydrochloric acid system for analytical separations, several variables were studied. It is apparent from the distribution coefficients listed in Table 2 that the majority of elements studied, in a system such as 50% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid, fall into two categories; those which are strongly sorbed by the resin and those which are only very slightly sorbed if at all. Thus, if column behavior can be predicted from distribution coefficients, the separation of the metals in the sorbed group from those in the non-sorbed group appears obvious. What is not obvious however is how any separations within either major classification could be effected. One possible means of varying the distribution coefficient of some of the metals studied would be to increase the acid concentration in the solvent system employed. To observe the effect of this increase, distribution coefficients were determined for cobalt(II), lead(II), titanium(IV), zirconium-(IV), and iron(III) in 20% dimethyl sulfoxide-methyl alcohol-hydrochloric acid where the acid strength was varied from 1.21M to 9.07M in the system. The distribution coefficients determined are listed in Table 6.

Table 6. Distribution coefficients for 5 metals on Amberlyst XN-1001 resin from 20% dimethyl sulfoxide-methyl alcohol-hydrochloric acid solutions as a function of acid strength

Molarity of HCl (percent of HCl)	Co(II)	Pb(II)	Ti(IV)	Zr(IV)	Fe(III)
1.21M (10%)	426	747	~0	~0	6.5
2.42M (20%)	293	338	~0	~0	16
3.62M (30%)	211	168	~0	~0	47
4.85M (40%)	155	67	~0	~0	142
6.05M (50%)	117	22	0.39	~0	443
7.25M (60%)	87	7.0	0.80	1.6	1631
8.45M (70%)	71	3.2	1.9	6.5	5426
8.65M (72%)				8.4	
9.07M (75%)	61	1.9	3.0		

It is evident that the behavior of metals in systems containing hydrochloric acid in concentrations much greater than 1.0M is no longer explained by the sorption of neutral complexes. At very high concentrations of hydrochloric acid, metallic behavior is quite accurately predicted from the data of Kraus and Nelson (2,3) in aqueous systems because the formation and stability of the chloride complexes predominates over any effect of a nonaqueous solvent in the system. Increasing the acid concentration is shown to be a useful means of raising, if only slightly, the distribution coefficients of titanium(IV), zirconium(IV), and iron(III). Although they were not determined, the distribution coefficients of molybdenum(VI) would be expected to increase rather markedly with increases in the hydrochloric acid concentration in the system.

The Effect of Water on the Behavior of Selected Metals

The effect of added water on the distribution coefficients of elements retained by an anion exchanger in 50% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid was demonstrated. This study was carried out in two stages. First the distribution coefficients for copper(II), cobalt-

(II), zinc(II), cadmium(II), and lead(II) were measured in 30% dimethyl sulfoxide-methyl alcohol-hydrochloric acid where the concentration of hydrochloric acid was lowered from 0.6$\underline{M}$ to less than 0.001$\underline{M}$ by the addition of water to replace the hydrochloric acid in the system. The results of these determinations are listed in Table 7. Although the addition of small amounts of water had different effects on copper(II) and cobalt(II) than it did on the other three elements, the distribution coefficients of neither copper nor cobalt were reduced to usefully low values for elution purposes.

Table 7. Effect of water on the distribution coefficients of 5 metals onto Amberlyst XN-1001 resin from 30% dimethyl sulfoxide-methyl alcohol-hydrochloric acid systems

Molarity of HCl	n_{DMSO}	Cu(II)	Co(II)	Zn(II)	Cd(II)	Pb(II)
0.61	0.175	183	307	736	941	388
0.48	0.174	158	233	803	721	411
0.36	0.174	135	168	970	758	433
0.24	0.173	101	100	1074	922	462
0.12	0.173	63	46	1597	1265	390
<0.01	0.172	6.6	2.1	2644	738	-

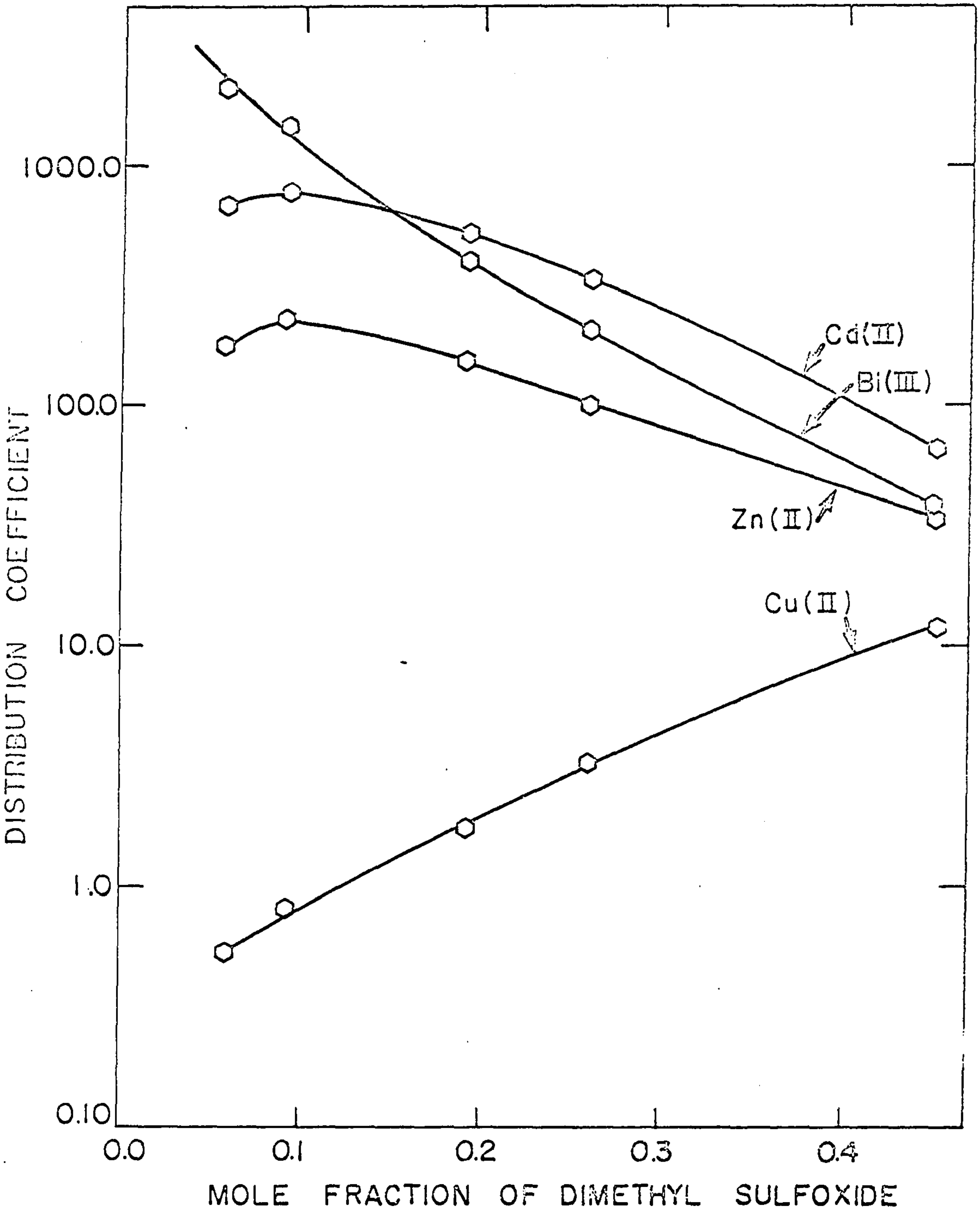
A second series of data were determined in a dimethyl sulfoxide-water-0.6$\underline{M}$ hydrochloric acid system where the amount of water added was varied from 20 to 80% while the dimethyl sulfoxide in the system was decreased proportionally.

Distribution coefficients for copper(II), cobalt(II), cadmium(II), zinc(II), and bismuth(III) were run in this system, and these are listed in Table 8. A plot of the logarithm of the distribution coefficients against the mole fraction of dimethyl sulfoxide is given in Figure 5. From this second series of distribution coefficients it is clear that copper and cobalt can be separated from cadmium, zinc, and bismuth using dimethyl sulfoxide-0.6M hydrochloric acid containing 70 to 80% water, after elution of the non-sorbed group of elements with 50% dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid.

Table 8. Distribution coefficients of 5 metals onto Amberlyst XN-1001 resin from dimethyl sulfoxide-water-0.6M hydrochloric acid systems

% H_2O	% DMSO	n_{DMSO}	Cu(II)	Co(II)	Cd(II)	Zn(II)	Bi(III)
20	80	0.45	12	1.7	66	34	44
40	60	0.26	3.3	~ 0	332	100	207
50	50	0.19	1.8	~ 0	520	152	386
70	30	0.09	0.81	~ 0	765	225	1433
80	20	0.06	0.54	~ 0	679	176	2094

Fig. 5. Distribution coefficients of four metal chlorides as a function of the mole fraction of dimethyl sulfoxide in a system of dimethyl sulfoxide-water-0.6M hydrochloric acid on Amberlyst XN-1001 resin


1000.0
100.0
10.0
1.0
0.10
DISTRIBUTION COEFFICIENT
0.0
0.1
0.2
0.3
0.4
MOLE FRACTION OF DIMETHYL SULFOXIDE
Cd(II)
Bi(III)
Zn(II)
Cu(II)

SEPARATIONS

The ultimate test of the usefulness of a new solvent system for anion exchange chromatography lies in its applicability to actual column separations. Since in many cases there are several recognized ion exchange procedures for the separation of two metals, a new system, to be useful, must possess some obvious advantages over existing methods. The primary objectives of any analytical separation procedure are that it be simple, rapid, and complete. In the case of separations carried out by ion exchange techniques conditions should be selected such that while one component is strongly sorbed by a very short column of resin, the second is eluted almost with the solvent front so that the separation may be performed quickly utilizing a fast flow rate. It should then be possible to strip the sorbed metal from the column using a minimum of eluent. This situation is seldom achieved in ion exchange, and especially not in ion exchange where mixed solvent systems are used. In these latter cases flow rates are usually necessarily slow (less than 0.5 ml./min.) because equilibrium rates are slower in mixed systems than they are in aqueous systems.

The merits of the dimethyl sulfoxide-methyl alcohol-0.6<u>M</u>

hydrochloric acid system for use with a macroreticular anion exchange resin for the separation of metals become obvious when viewed in terms of the above criteria. Numerous separations were performed utilizing the mixed solvent system. Even for the resolution of four-component mixtures, a column length of 10 cm. proved totally adequate, because under the conditions of elution, metals not eluted remained in tight bands at the top of the column for the duration of the separations. In addition, the flow rate of the eluent through the column was at no time reduced below 1 ml./min., a considerable improvement over existing techniques.

The actual efficiency of a column of ion exchange resin in the dimethyl sulfoxide-methyl alcohol-0.6<u>M</u> hydrochloric acid system may be evaluated through application of the plate theory (5). To apply these principles the column is assumed to be composed of a large number of theoretical plates, within each of which equilibrium is reached between the metal in the resin and in the solution phases. A column characterized by a small number of theoretical plates would possess major limitations for analytical separations. For metals with distribution coefficients of less than 100, several equilibrations would be necessary for extraction from the liquid phase. Ideally the extracted species should be retained within the top-most portion of the resin bed, and this may occur only if the height equivalent of a theoretical plate (HETP) is small.

The determination of the number of theoretical plates in a column of resin is thus a useful means of characterizing the efficiency of a column to perform a separation. The calculation of the number of theoretical plates (N') in a column packed with resin is most easily made from a carefully plotted elution curve. Once plotted, the parameters $\bar{v}$ and β may be defined, where $\bar{v}$ is the peak elution volume or the volume of eluent required to elute the maximum of the elution band, and β is the height of the peak at its maximum divided by e, the base of the natural logarithm system. The relationship between these parameters and the number of theoretical plates is the following.

$$N' = 8\left(\frac{\bar{v}}{\beta}\right)^2$$

From the value of N' determined for a particular column and a knowledge of the height of the column, one can calculate the HETP of the column and use this value to characterize the ion exchange system. This calculation was made for the dimethyl sulfoxide-methyl alcohol-0.6<u>M</u> hydrochloric acid system using nickel(II) as the eluted species. The elution curve is given in Figure 6. From this curve a value for $\bar{v}$ was determined to be 14.8 ml. and the value of β was determined to be 0.0031. From these parameters the value of N' for the 8.9 cm. column was calculated to be 35.6 and the HETP was then determined to be 0.25 cm. Since this parameter has not been computed for other mixed solvent systems described in the literature there are no data available for comparison.

The column separations actually performed are summarized in Table 9. Without exception they are illustrative of the usefulness of the dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid mixed solvent system. The initially eluted element, in all cases, was completely eluted in a collected volume of 25 to 30 ml. including the sample volume (usually 5 to 10 ml.) at a flow rate of 1 ml./min. Following this the retained element, in the case of two-component separations, was rapidly stripped from the column thus enabling an efficient and complete separation. This process is illustrated by separations I through XII listed in Table 9.

The usefulness of the addition of water to the dimethyl sulfoxide-hydrochloric acid system is illustrated by separations XIII through XV. In these cases it was possible to

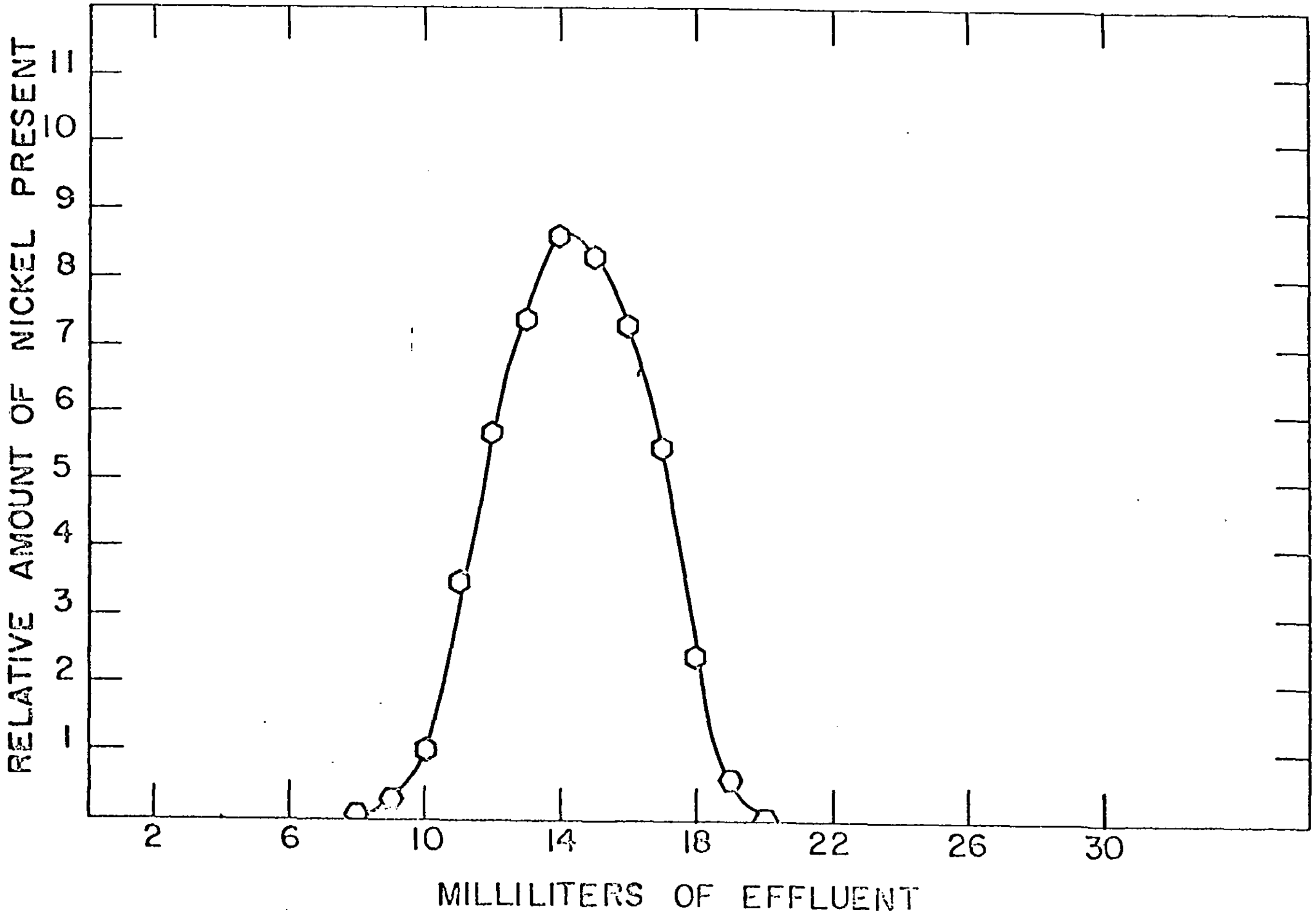


Fig. 6. Elution curve for nickel(II) from an 8.9 cm. column of Amberlyst XN-1001 resin using 50% dimethyl sulfoxide-methyl alcohol-0.6$\underline{M}$ hydrochloric acid

select conditions such that cobalt(II) was rapidly eluted from a column while bismuth(III), zinc(II), and lead(II) were tightly retained, thus enabling the separation of cobalt from the other three elements. The value of varying the hydrochloric acid concentration in the dimethyl sulfoxide-methyl alcohol-hydrochloric acid system is illustrated in separations XVI and XVII. In these cases molybdenum(VI) was quantitatively separated from titanium(IV) and from zirconium(IV) where in a dimethyl sulfoxide-methyl alcohol-0.6$\underline{M}$ hydrochloric acid system all three elements would be eluted simultaneously with the solvent front. Separations XVIII through XXVII are illustrative of the application of the dimethyl sulfoxide-methyl alcohol-0.6$\underline{M}$ hydrochloric acid system to the resolution of mixtures which must be prepared by dissolution prior to analysis. In every case these separations are rapid, simple, and quantitative demonstrating the flexibility of the mixed solvent system which has been developed.

Table 9. Anion exchange separations of metal ions using dimethyl sulfoxide-methyl alcohol-hydrochloric acid systems with Amberlyst XN-1001 resin

Separation		Eluent	(ml.) Vol.	Column length	mmoles. Added	mmoles. Found	Error
I	a. Ti(IV)	30% DMSO-MeOH-0.6$\underline{M}$ HCl	25	9 cm.	0.0514	0.0519	+0.97%
	b. Co(II)	H_2O	30	--	0.0502	0.0503	+0.20%
II	a. Ni(II)	30% DMSO-MeOH-0.6$\underline{M}$ HCl	20	9 cm.	0.0550	0.0552	+0.36%
	b. Co(II)	H_2O	25	--	0.0489	0.0489	0.00%
III	a. Ti(IV)	30% DMSO-MeOH-0.6$\underline{M}$ HCl	25	9 cm.	0.0482	0.0475	-1.04%
	b. Zn(II)	0.005$\underline{M}$ HCl	40	--	0.0497	0.0495	-0.40%
IV	a. Ni(II)	30% DMSO-MeOH-0.6$\underline{M}$ HCl	20	9 cm.	0.0548	0.0549	+0.18%
	b. Zn(II)	0.005$\underline{M}$ HCl	40	--	0.0497	0.0495	-0.40%
V	a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	30	9 cm.	0.0557	0.0554	-0.54%
	b. Pb(II)	8$\underline{M}$ HCl	50	--	0.0486	0.0486	0.00%
VI	a. Ti(IV)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	30	9 cm.	0.0443	0.0448	+1.13%
	b. Pb(II)	8$\underline{M}$ HCl	40	--	0.0502	0.0501	-0.20%
VII	a. Zr(IV)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	40	9 cm.	0.0544	0.0543	-0.18%
	b. Co(II)	H_2O	25	--	0.0526	0.0525	-0.19%
VIII	a. Zr(IV)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	40	9 cm.	0.0536	0.0532	-0.75%
	b. Pb(II)	8$\underline{M}$ HCl	40	--	0.0476	0.0477	+0.21%

Table 9. (Continued)

Separation		Eluent	(ml.) Vol.	Column length	mmoles. Added	mmoles. Found	Error
IX	a. Ni(II)	50% DMSO-MeOH-0.6M HCl	30	9 cm.	0.0559	0.0560	+0.18%
	b. Bi(III)	1M H_2SO_4	70	--	0.0497	0.0498	+0.20%
X	a. Zr(IV)	50% DMSO-MeOH-0.6M HCl	50	9 cm.	0.0549	0.0548	-0.18%
	b. Bi(III)	1M H_2SO_4	70	--	0.0497	0.0497	0.00%
XI	a. Mo(VI)	50% DMSO-MeOH-0.6M HCl	30	9 cm.	0.0500	0.0500	0.00%
	b. Pb(II)	8M HCl	50	--	0.0483	0.0483	0.00%
XII	a. Mo(VI)	50% DMSO-MeOH-0.6M HCl	30	9 cm.	0.0500	0.0500	0.00%
	b. Bi(III)	1M H_2SO_4	70	--	0.0499	0.0498	-0.20%
XIII	a. Co(II)	DMSO-80% H_2O-0.6M HCl	30	7.5 cm.	0.0527	0.0528	+0.19%
	b. Bi(III)	1M H_2SO_4	70	--	0.0485	0.0485	0.00%
XIV	a. Co(II)	DMSO-80% H_2O-0.6M HCl	30	7.5 cm.	0.0527	0.0527	0.00%
	b. Zn(II)	0.005M HCl	40	--	0.0504	0.0504	0.00%
XV	a. Co(II)	DMSO-80% H_2O-0.6M HCl	30	7.5 cm.	0.0528	0.0527	-0.19%
	b. Pb(II)	8M HCl	50	--	0.0494	0.0494	0.00%
XVI	a. Ti(IV)	20% DMSO-MeOH-4.85M HCl	25	7.5 cm.	0.0650	0.0646	-0.62%
	b. Mo(VI)	50% DMSO-MeOH-0.6M HCl	30	--	0.0500	0.0500	0.00%
XVII	a. Zr(IV)	20% DMSO-MeOH-4.85M HCl	25	7.5 cm.	0.0535	0.0537	+0.37%
	b. Mo(VI)	50% DMSO-MeOH-0.6M HCl	30	--	0.0500	0.0502	+0.40%

Table 9. (Continued)

Separation	Eluent	(ml.) Vol.	Column length	mmoles. Added	mmoles. Found	Error
XVIII a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.7970	0.7980	+0.13%
b. Cu(II)	H_2O with H_2O_2	50	--	0.1650	0.1660	+0.61%
XIX a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.8704	0.8701	-0.03%
b. Cu(II)	H_2O with H_2O_2	50	--	0.2172	0.2168	-0.18%
XX a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.9740	0.9740	0.00%
b. Co(II)	H_2O	50	--	0.2100	0.2120	-0.95%
XXI a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.6796	0.6788	-0.12%
b. Co(II)	H_2O	50	--	0.3530	0.3543	+0.37%
XXII a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.8550	0.8550	0.00%
b. Pb(II)	8$\underline{M}$ HCl	50	--	0.3080	0.3110	+0.97%
XXIII a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.7324	0.7321	-0.04%
b. Pb(II)	8$\underline{M}$ HCl	50	--	0.0854	0.0853	-0.12%
XXIV a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	50	13 cm.	0.7069	0.7068	-0.01%
b. Pb(II)	8$\underline{M}$ HCl	50	--	0.2881	0.2881	0.00%
XXV a. Ni(II)	50% DMSO-MeOH-0.6$\underline{M}$ HCl	30	10 cm.	0.7500	0.7480	-0.27%
b. Pb(II)	8$\underline{M}$ HCl	40	--	1.0340	1.0360	+0.19%
c. Co(II)	1$\underline{M}$ HCl	30	--	1.1060	1.0960	-0.90%
d. Bi(III)	1$\underline{M}$ H_2SO_4	80	--	1.0580	1.0560	-0.19%

Table 9. (Continued)

Separation		Eluent	(ml.) Vol.	Column length	mmoles. Added	mmoles. Found	Error
XXVI	a. Ni(II)	50% DMSO-MeOH-0.6M HCl	30	10 cm.	0.7500	0.7500	0.00%
	b. Pb(II)	8M HCl	40	--	1.0340	1.0340	0.00%
	c. Co(II)	1M HCl	30	--	1.1060	1.1000	-0.54%
	d. Bi(III)	1M H_2SO_4	80	--	1.0580	1.0560	-0.19%
XXVII	a. Ni(II)	50% DMSO-MeOH-0.6M HCl	30	10 cm.	0.8160	0.8180	+0.25%
	b. Pb(II)	8M HCl	40	--	1.2140	1.2160	+0.16%
	c. Co(II)	1M HCl	30	--	0.9840	0.9820	-0.20%
	d. Zn(II)	.001M HCl	50	--	1.1240	1.1220	-0.18%

SUMMARY

The effect of dimethyl sulfoxide on the anion exchange behavior of many metals in a methanolic system with hydrochloric acid was explored. Distribution coefficients for 26 elements were determined in a mixed solvent system of dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid where the proportions of dimethyl sulfoxide and methyl alcohol were varied. From a graphical interpretation of these data, a theoretical explanation of the effects of dimethyl sulfoxide on the distribution coefficients was made. The role of the dielectric constant of the solvent mixture in influencing the distribution characteristics of a metal was considered through comparison of the behavior of copper(II) in dimethyl sulfoxide-methyl alcohol-0.6M hydrochloric acid, dimethyl sulfoxide-acetone-0.6M hydrochloric acid, and dimethyl sulfoxide-tetrahydrofuran-0.6M hydrochloric acid systems where the proportions of dimethyl sulfoxide present were varied from 20 to 100%. As a means of enhancing the analytical usefulness of the dimethyl sulfoxide system, the effects of the addition of water, and of the variation in acid strength on the distribution coefficients of selected metals were studied.

Finally, as a measure of the analytical usefulness of the dimethyl sulfoxide-methyl alcohol-hydrochloric acid mixed solvent system in anion exchange, 27 separations of 2- and 4-component mixtures were carried out, each with quantitative results. The combination of the versatility of the solvent system as exemplified by the inclusion of silver(I) and lead(II) in the list of metals studied, the speed of separation, and the short columns required for even the 4-component separations serve to emphasize the significance of the dimethyl sulfoxide-methyl alcohol-hydrochloric acid mixed solvent system as the method of choice for the anion exchange separations of many metal mixtures.

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