The Synerqistic Solvent Extraction of Manganese by Macrocyclic Crown Ethers in Combination with Didodecylnaphthalene Sulfonic Acid: Effect of Macrocycle Substituents

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THE SYNERGISTIC SOLVENT EXTRACTION OF MANGANESE BY MACROCYCLIC CROWN ETHERS IN COMBINATION WITH DIDODECYLNAPHTHALENE SULFONIC ACID: EFFECT OF MACROCYCLE SUBSTITUENTS*

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ABSTRACT

Crown ethers in combination with organophilic cation exchangers synergize the extraction of certain metal ions from aqueous solutions, and their selectivity has been thought largely dependent on the correspondence between the crown ether's cavity diameter and the metal ion diameter. This work focuses on two crown ethers, *tert.*-butylbenzo -15-crown-5 (*t*BB15C5), and *tert.*-butylcyclohexano -15-crown-5 (*t*BC15C5) each of which has a cavity diameter of 1.7 to 2.2 X 10^{-10} m, and their extraction of Mn^{2+} (ionic diameter 1.4 to 2.2 X 10^{-10} m) from aqueous nitrate solutions. The organophilic cation exchanger used was didodecylnaphthalene sulfonic acid (HDDNS). The data show no observable complexes of the manganese salt of HDDNS

with the benzo-substituted crown, $tBB15C5$, but the cyclohexano-substituted crown, $tBC15C5$, forms a strong complex with $Mn(DDNS)_2$. The system $tBC15C5/HDDNS$ is an effective phase-transfer agent for manganese. Since the cavities in the two crown ethers are the same size, it appears that the differences observed between the benzo- and cyclohexano-substituted crowns are due to their different substituents.

INTRODUCTION

Crown ethers in synergistic combination with organophilic cation exchangers are known to function as effective solvent extraction systems for metal ions. [1] The selectivity of crown ethers for certain metals has often been shown to depend strongly on the correspondence between the crown ether cavity size and the metal ion diameter (Ref. 2-5, for example). However, recent publications report that substituents on the crown ether ring also affect the strength of complexation. [5-10] In particular, thermochemical and ultrasonic relaxation measurements show that alkyl or aryl substituents on the crown ether ring produce differences in selectivity in the interaction of macrocycles with metal salts in homogeneous solutions. [6,7,9] Further, extractions of metal ions from aqueous nitrate solutions by organic solutions of organophilic acids in combination with organophilic crown ethers also show effects apparently due to crown ether substituents. [7,10]

This study has focused on two crown ethers, $tert$.-butylbenzo-15-crown-5 ($tBB15C5$) and $tert$.-butylcyclohexano-15-crown-5 ($tBC15C5$), in combination with didodecylnaphthalene sulfonic acid (HDDNS) in toluene solution as extractants of manganese from aqueous nitric acid solutions. The crown ethers have cavity diameters in the range 1.7 to 2.2×10^{-10} m and the Mn^{2+} ion has a diameter of 1.4 to 2.2×10^{-10} m, depending on its coordination number. [11] Previous references to crown ether complexes with manganese are few. Vance et al., report an 18-crown-6 compound with manganese with coordination to 6 water molecules. [12] Farago reports on a benzo-14-crown-5 compound in which the crown ether is directly bonded to manganese. [13] The purpose of this work is to examine the differences in manganese complexation by benzo- and cyclohexano-substituted 15-crown-5 in an extraction system in which the sulfonic acid HDDNS is the cation exchange extractant.

TREATMENT OF DATA

A general equation for the extraction of metal ions by a synergistic combination of crown ether and sulfonic acid can be written: [14]

$$M^{i+} + \frac{n}{y}(HA)_y + mB \longrightarrow \frac{1}{x}(MA_i \cdot (n-i)HA \cdot mB)_x + iH^+ \qquad (1)$$

where, M = metal ion and i = the charge on that ion.
HA = sulfonic acid and y = aggregation number of HA.
n = number of acid anions in the complex formed.
B = the crown ether.
m = the number of crown ethers in the complex formed.
x = the number of complex molecules in an aggregate.

EXPERIMENTAL

Reagents:

The crown ethers were obtained from Parish Chemical Company, Orem, Utah. They were stated to be 99% pure and were used without further purification. Solutions of these compounds were prepared gravimetrically.

Didodecylnaphthalene sulfonic acid was obtained from King Industries, Norwalk, CT as a 40% solution in heptane. The heptane was removed with a rotary evaporator, and the resulting material was purified by an ion-exchange method developed by Danesi, Chiarizia, and Scibona for dinonylnaphthalene sulfonic acid. (14) The purified material was dissolved in toluene and standardized by titration in ethyl alcohol with aqueous NaOH. The diluent used for all organic solutions was reagent grade toluene.

The radionuclide, manganese-54, was obtained from New England Nuclear in 0.1 M HCl. The solution was evaporated to dryness and the residue redissolved in 0.01 M nitric acid.

All other chemicals used were obtained from commercial sources and were of reagent grade or better.

Equipment and Procedures:

All sample solutions were made by dilution of stock solutions of known concentration. Manganese concentration in all initial aqueous phases was 5×10^{-5} M, in 0.2 M HNO3 each containing sufficient manganese-54 to insure accurate counting of the low phase after equilibration. Two mL of each phase was placed in a 5-mL vial and equilibrated by repeated inversion on a rotating device at room temperature (23±2 ^{o}C) for 1 hour, a length of time found to be more than adequate to attain equilibrium.

After equilibration, samples were allowed to settle for approximately 10 min. Then 1 mL of each phase was removed and counted in a 3-in

well-type Na(Tl)I crystal, the spectrum being collected on a multichannel analyzer.

Vapor pressure osmometry measurements were made using a Corona-Wescan vapor pressure osmometer. Measurements were made vs. a 0.1 M solution of sucrose octaacetate on the reference thermistor and in the atomsphere-saturating cup. The solutions were all water-saturated. The equation for the conditional equilibrium constant (assuming the activity coefficient quotient is constant) would then be given by:

$$K = \frac{[(MA_i \cdot (n-i) HA \cdot mB)_x]^{\frac{1}{x}}}{[(M^{i+})][(HA)_y]^{\frac{n}{y}} [B]^m} [H^+]^i \qquad (2)$$

If the value of x is 1; i.e., the metal complex product does not aggregate and is therefore mononuclear in M, the distribution coefficient, D (D = [M]org./[M]aq.) can be substituted for the first term in the numerator divided by the first term in the denominator of equation (2) yielding:

$$K = \frac{D[H^+]^i}{[(HA)_y]^{\frac{n}{y}} [B]^m} \qquad (3)$$

This equation can be manipulated to give:

$$logK = logD + ilog[H^+] - \frac{n}{y}log[(HA)_y] - mlog[B] \qquad (4)$$

from which, with distribution data taken at low loading, it is possible to determine the coefficients n, m and i by simple graphical means providing (1) y is known, (2) there is no interaction between HA and B, and (3) there is a single predominant organic-phase complex species. If these conditions are met, then by selectively holding all reagent concentrations but one constant in Eq. 4, the coefficient of the varied reagent may be determined from the slope of a log-log plot of D vs the varied reagent concentration.   However in this case and many others, complications arise because of self-association of the reagent and by its association with other soluble species.   With such complications, computer-aided analysis of the distribution data is desirable if not necessary. An interactive non-linear least squares program called SXLSQ has been developed(15) that allows various combinations of reactants and products and their coefficients to be tested by calculating conditional (assuming constant activity coefficient quotient)

equilibrium constants. The set of reactant and product species that produce the best agreement between the calculated and observed distribution data is then chosen from those tested.

RESULTS AND DISCUSSION

Vapor Pressure Osmometry:

Figure 1 shows the results of vapor pressure osmometry measurements of solutions of the crown ethers mixed with HDDNS. The total reagent concentration for each point was held constant at 0.1 M, while the percent crown ether was varied from zero (100% HDDNS) at the left to 100% (0% HDDNS) at the right of the plot. The lines drawn on fig 1 are the result of a simultaneous least-squares fit to this data and the extraction data.

The particle concentrations for HDDNS alone (points at the left of the plot) indicate a 7- to 10-fold aggregation of this material in solution. In both cases the crown ether appears to be a monomer, although it is clear that there is interaction between the HDDNS and both crown ethers, stronger in the case of tBC15C5. The values for the aggregation of HDDNS are reasonably consistent with those found for the same compound in carbon tetrachloride. (17) However, subsequent measurements on the same and different batches of HDDNS in our laboratory have given values for the aggregation number ranging from 3 to 10. In addition, Kuvaeva et al. (18) found the degree of aggregation of HDDNS in benzene at 25°C in wet and dry benzene to be 4 and 3.5 respectively. The reason for this variability in the measured aggregation number for HDDNS is not known at this time. In our laboratory, the proper operation of the vapor pressure osmometer was verified with standard neutral compounds. However, the possibility of low-molecular-weight impurities in the HDDNS has not been eliminated although the material was purified.

In a previous publication describing the program SXLSQ(15) the present data were reported consistent with HDDNS association numbers greater than 8 with any number, no matter how large, giving a good fit if appropriate product compositions were chosen. In presenting the fitting results here we have chosen an association number of 9 for HDDNS, a value near the average of our measured values and in reasonable agreement with values found by others. (17, 18) The best choices of a minimum number of species required to account for the extraction data are presented later in this section.
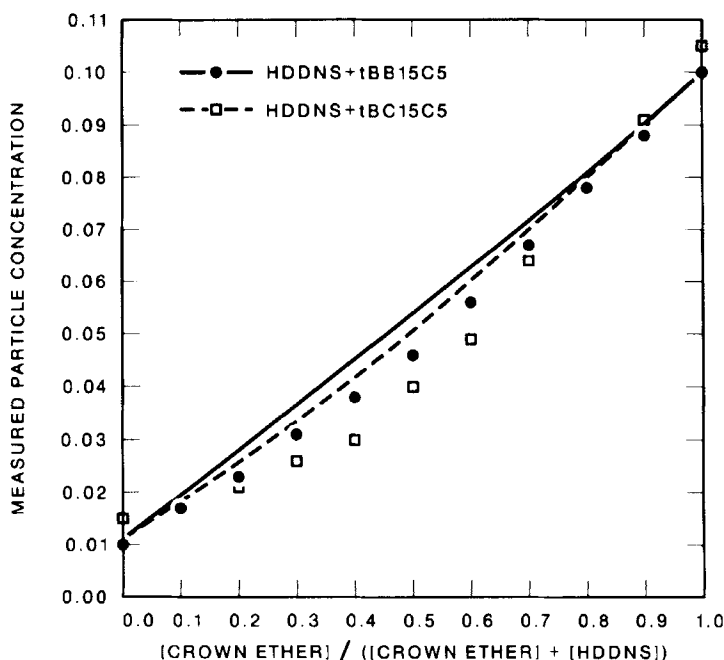
FIG. 1. Particle Concentrations Obtained by Measurements With a Vapor-Pressure Osmometer. Mixtures of HDDNS and *t*BB15C5 (●) and *t*BC15C5 (○) at a total concentration of 0.1 *M* but varying ratio in the diluent toluene. The lines are from the least-squares fit to these data and the extraction data.

Loading Curve:

Figure 2 shows the loading (equilibrium) curves for manganese extraction from 0.2 *M* nitric acid by a toluene solution of 0.025 *M* crown ether and 0.075 *M* HDDNS. Curves for both of the crown ethers are shown.

Both curves show a slope of approximately 1 below a manganese concentration of 1×10^{-4}. If the concentration of nitric acid and of free HDDNS and crown ether are constant, as they virtually are in this region, then it is permissible to write equation 2 with X = 1. The logarithmic form of equation 2 can then be written as below.

$$log(MA_i(n-i)HA \cdot mB) =$$

$$log[M^{i+}] + \frac{n}{y}log[(HA)_y] + mlogB - ilog[H^+] + logK \qquad (5)$$
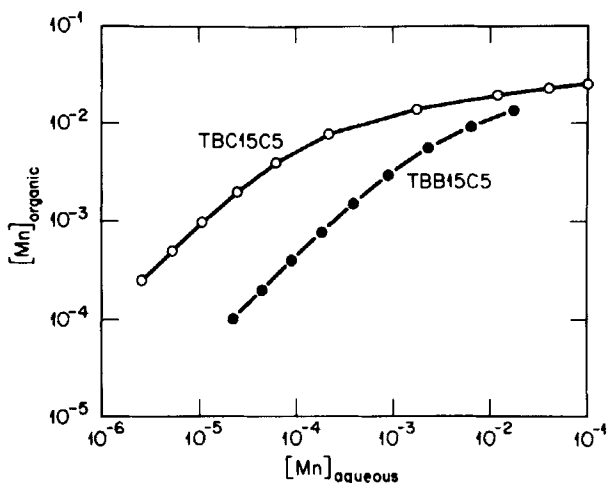
Fig. 2. The Concentration of Manganese in the Organic Phase as a Function of Its Equilibrium Concentration in 0.2 M Aqueous Nitric Acid. The organic phase was 0.075 M HDDNS and 0.025 M tBB15C5 (●) or tBC15C5 (O).

Then assuming the aqueous manganese to be ionic and mononuclear, as we believe it to be,   the ratio of organic to aqueous manganese concentration may be defined as a distribution coefficient having thermodynamic meaning in   interpting the extraction data.   Subsequent extraction experiments maintained manganese at or below this concentration in order to avoid any loading problems and to assure that there is no organic-phase self association of manganese.

Reagent Concentration Dependence:

Figure 3 shows the dependence of the distribution coefficient on the concentration of the crown ethers, at a constant HDDNS concentration of 0.1 M and constant aqueous nitric acid = 0.1 M.   The crown ether is believed not to aggregate but does react with HDDNS.   Thus, for graphical interpretation methods we do not know the concentration of free B; however, if the interaction between B and HDDNS is assumed weak we can, perhaps, still consider B monomeric.   If equation 4 is written as:

$$log\ D\ =\ m\ log[B]\ +\ logK'\qquad\qquad(6)$$

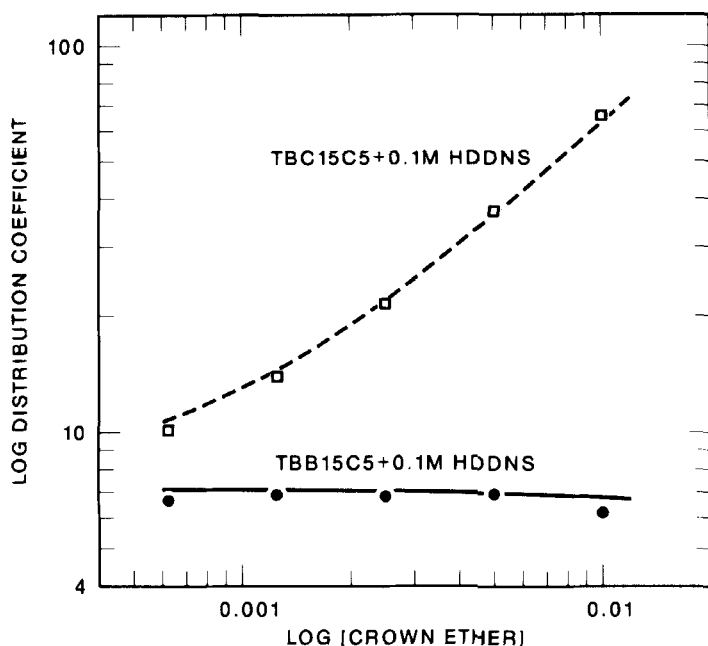slope interpretation suggests that tBB15C5 (slope = 0) does not interact

Fig. 3. The Distribution Coefficient of Manganese as a function of the
Concentration of tBB15C5 (●) or tBB15C5 (○) in Toluene with the
Concentration of HDDNS Constant at 0.1 M. The lines are from the fit
to the general model using all the data.

with manganese. With tBC15C5, a slope of 0.7 is obtained suggesting
complex formation with tBC15C5 approaching one crown ether per
manganese. From least-squares fitting (to be presented later) of this data
along with other data, species containing the salt $Mn(DDNS)_2$, the acid
form, HDDNS (amount depending on its degree of aggregation) and a
single tBC15C5 gave good fits.

Figure 4 shows the dependence of the distribution coefficient on the
concentration of HDDNS; with no crown ether present, with 0.1 M
tBB15C5 present, and with tBC15C5 present. The pertinent equation in
this case is:

$$logD = \frac{n}{y}log[(HA)_y] + logK' \qquad (7)$$

In the extraction with HDDNS alone, a slope of 1.1 suggests that the
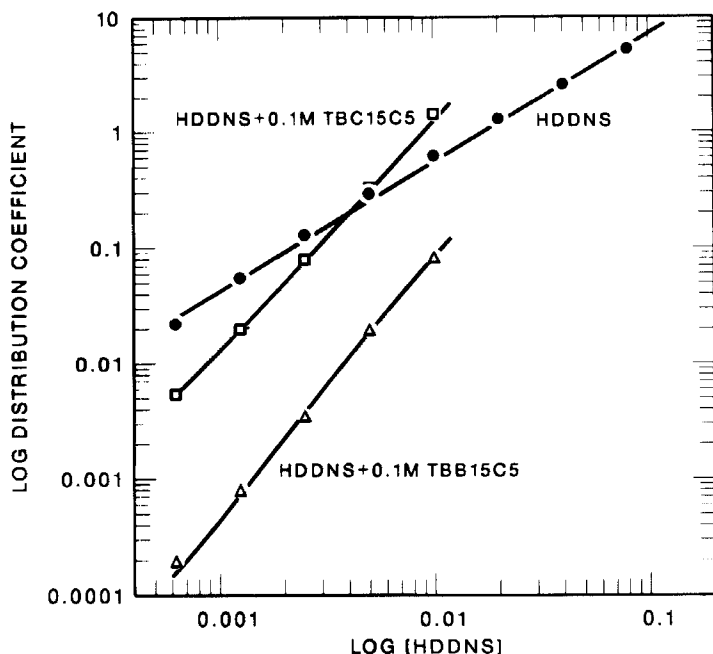manganese ion simply attaches to the HDDNS micelle in the organic phase

Fig. 4. The Distribution Coefficient of Manganese as a Function of HDDNS Concentration With no Crown Ether present (Δ), With 0.10 M tBB15C5 Present (●) and With 0.10 M tBC15C5 Present (○). The lines are from the fit to the general equation.

and that the number of acid monomers in the complex is approximately that in the micelle. In the case where tBB15C5 was present at constant 0.1 M a slope of 2.1 is obtained. Since the data in figure 3 suggest little if any interaction between this crown and manganese, the higher slope for the dependence of D_{Mn} on tBB15C5 requires some explanation based on an interaction between tBB15C5 and HDDNS. One possibility is that the interaction results in some deaggregation of the sulfonic acid. Other researchers have found similar results using dinonylnaphthalene sulfonic acid and other coordinating agents.(19-21) In the curve in which the concentration of tBC15C5 is held constent at 0.1 M and the concentration of HDDNS is varied, a slope of approximately 2 was also obtained. Again, a possible interpretation is deaggregation of the HDDNS by the crown ether and the formation of a Mn/HDDNS/tBC15C5 complex containing, on the average, two of the deaggregated HDDNS species. Least-squares fitting of the data was also found to require reactions between the crown ethers and HDDNS that result in deaggregation of the HDDNS. Under the conditions of
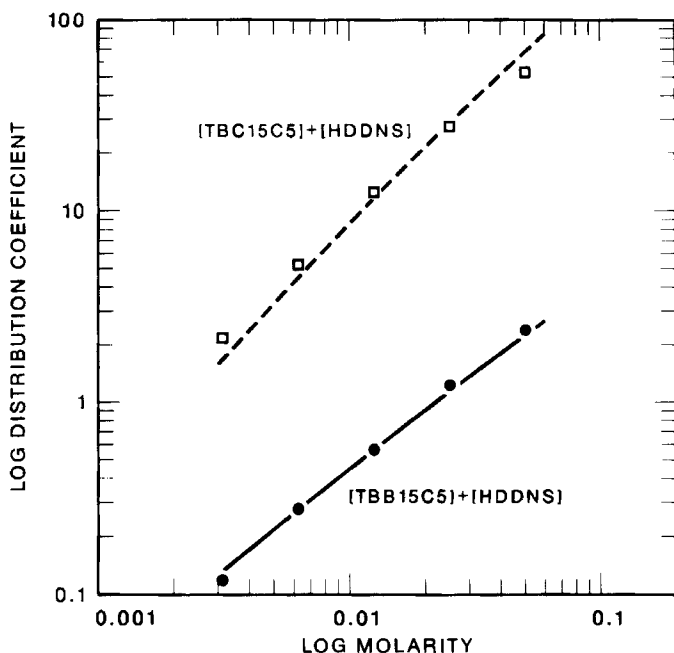
Fig. 5. The Distribution Coefficient of Manganese as a Function of Reagent Concentration at a Constant 1:3 Ratio of Crown Ether to Sulfonic Acid. The lines represent the fit to the general model.

the experiments shown in figure 3 in which the crown ether was present in excess over most of the [HDDNS] variation this reaction could have modified a substantial part of the HDDNS species even though the equilibrium constants are small.

In figure 5 the mole ratio of crown ether to HDDNS was 1.0 and the total reagent concentration was varied.   Results are shown with both tBB15C5 and with tBC15C5.   A slope of approximately one was obtained in both cases.   The straight lines are usually taken to suggest that there is a single predominant Mn species in the organic phase over the concentration range examined.   This conclusion is consistent with the results of least squares fitting.   The lines are those obtained from fitting to the model.

Continuous Variation
     Figure 6 shows data obtained for the extraction of manganese while maintaining the total crown ether + HDDNS concentration   constant at 0.1
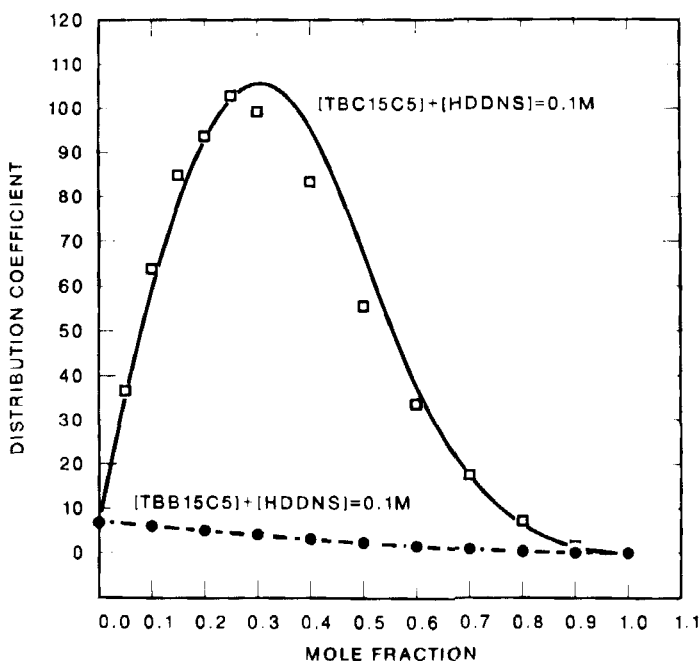
Fig. 6. Distribution Coefficient for Manganese as a Function of the Ratio [Crown Ether]/([HDDNS] + [Crown Ether]), the Total Being Constant at 0.1 M. The lines are from the fit to the general model.
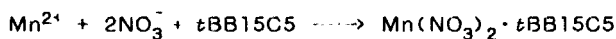
M but varying their ratio. (22) At the origin of each plot, the organic phase is 0.1 M HDDNS and at the right side it is 0.1 M crown ether. The aqueous phase was 0.2 M HNO$_3$. The curve with tBB15C5 shows again that there is no synergism in this system. The curve with tBC15C5 shows a maximum at 0.25 mole fraction (reagents only) of tBC15C5. Obviously, this is the composition one should use for the maximum extraction of manganese; however, because the HDDNS is known to be aggregated and to interact with the crown ether, this maximum can not be interpreted as a direct representation of the ratio of crown ether to HDDNS in the organic phase complex with manganese. Whereas the direct interpretation of Fig. 6 would indicate a complex containing one crown ether and three sulfonic acid molecules for each manganese, the least-squares fitting of all the extraction equilibrium data and VPO data, Figures 1 through 6, fit best with a complex having an average of ratio of one crown ether to six sulfonic acids.

Least-squares Fitting

Fitting the data to various models assuming HDDNS to be a 9-fold aggregate gave the reactions and equilibrium constants below, with a standard deviation of 2.08 times the 5% error estimated in the measured values of D. A minimum number of reactions consistent with a reasonable fit was used. The reaction of manganese nitrate with the crown ether was included to cover the obvious possibility but is relatively unimportant.

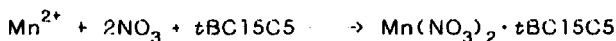$$Mn^{2+} + \frac{10}{9} (HDDNS)_9 \longrightarrow Mn(DDNS)_2 \cdot (HDDNS)_8 + 2H^+$$

$$\log K = 1.626$$

$$Mn^{2+} + 2NO_3^- + tBB15C5 \longrightarrow Mn(NO_3)_2 \cdot tBB15C5$$

$$\log K = -2.107$$

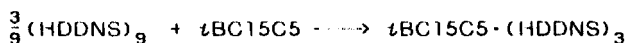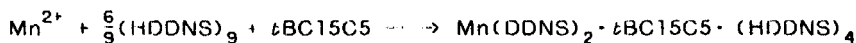$$\frac{4}{9} (HDDNS)_9 + tBB15C5 \longrightarrow tBB15C5 \cdot (HDDNS)_4$$

$$\log K = -0.040$$

The results of fitting the data on manganese extraction with the tBC15C5-HDDNS system are shown below. The reactions giving the best fit, along with their equilibrium constants, are given except that the reaction between manganese and HDDNS alone, being the same as presented in the previous set of equations, is not repeated. Estimated data error and standard deviation of fitting are the same as before.

$$Mn^{2+} + 2NO_3 + tBC15C5 \longrightarrow Mn(NO_3)_2 \cdot tBC15C5$$

$$\log K = -0.824$$

$$\frac{3}{9} (HDDNS)_9 + tBC15C5 \longrightarrow tBC15C5 \cdot (HDDNS)_3$$

$$\log K = 0.689$$

$$Mn^{2+} + \frac{6}{9}(HDDNS)_9 + tBC15C5 \longrightarrow Mn(DDNS)_2 \cdot tBC15C5 \cdot (HDDNS)_4$$

$$\log K = 4.018$$

CONCLUSIONS

The tBB15C5/HDDNS system does not exhibit synergistic extraction of manganese. The data indicate that extraction is due only to cation exchange with didodecylnaphthalene sulfonic acid. The manganese extracts in this system to form the salt $Mn(DDNS)_2$ in the organic phase with

additional HDDNS and probably some water attached.   The structure of the complex is unknown.   The interaction between HDDNS and crown ether is probably through hydrogen bonding.   Compounds have been reported between ethers, hydronium ions and acid anions. (23)

The tBC15C5/HDDNS solvent extraction system shows a synergistic enhancement of D_{Mn} over the sum of the distribution coefficients obtained with the two reagents used alone.   Thus, one must conclude that this cyclohexano-substituted crown does react with manganese and that the benzo substituent on tBB15C5 strongly inhibits the complexation of 15-crown-5 with manganese.   The effect of the nature of the constituent on the organic-phase coordinating ability of crown ethers that otherwise are formally identical allows an enhanced   range of selectivities for crown ethers as synergistic organic-phase coordinators.

Further, the tBC15C5/HDDNS system is unique in that it synergizes only manganese and zinc (and copper very slightly) of the first-row transition elements. (8)   Thus this extractant system has potential for use as a separation agent in analytical and process chemistry.

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