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DIMETHYLSULFOXIDE AUGMENTED CALCIUM ISOTOPE EFFECT WITH POLYMER-BOUND 18-CROWN-6 IN A CHROMATOGRAPHIC CHEMICAL EXCHANGE SYSTEM

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ABSTRACT

The enrichment of calcium isotopes with polymer-bound 18-crown-6 proceeds according to the following chemical exchange reaction:

$$^{40}Ca^{2+}_{(fluid)} + {}^{44}CaL^{2+}_{(solid)} \rightleftharpoons {}^{44}Ca^{2+}_{(fluid)} + {}^{40}CaL^{2+}_{(solid)}$$

where $L_{(solid)}$ represents 18-crown-6 bound to a polystyrene solid support. The separation coefficient, ϵ, for this exchange was found to be larger when dimethylsulfoxide (DMSO) was added to the fluid phase. When a fluid phase of 70% methanol and 30% chloroform (volume) is used as stock solution, ϵ=0.0035±0.0003 (for the ^{40}Ca-^{44}Ca isotope pair) after DMSO is added. DMSO was added to the extent of two and five volume percent. This compared to ϵ=0.0025±0.0002 without DMSO. The difference in the isotope effect is attributed to a change in the coordination sphere of the calcium solvate in the fluid phase.

The stability of the calcium-crown complex was reduced when DMSO was added. The binding constant of the calcium-crown complexation-decomplexation reaction was smallest when the higher concentration of DMSO was used. This was attributed to the formation of a calcium complex with DMSO in the fluid phase.

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INTRODUCTION

Macrocyclic compounds have been shown to engender large equilibrium isotope effects in chemical exchange with metal isotopes (1). It is of considerable interest to combine the large macrocycle isotope effect with chromatographic processes which have the large number of stages normally desirable for an isotope separation process. One strategy for accomplishing this is to chemically bind macrocycles to a solid support. This approach has advantages in that the reflux (column reconditioning) is straightforward, and process recycling of macrocycles is not necessary. The enrichment method used, displacement chromatography, is readily applicable to a continuous process.

Both polymer-bound [222] cryptand (2,3) and polymer-bound 18-crown-6 (3) have exhibited large isotope effects. While calcium chemical exchange with the cryptand yielded the larger separation coefficient, $\epsilon=0.0039\pm0.0003$ for the ^{44}Ca-^{40}Ca isotope pair, the exchange rate was too slow for practical application (3). Chemical exchange with the polymer-bound 18-crown-6 exhibited a smaller separation coefficient, $\epsilon=0.0025\pm0.0002$ for the ^{44}Ca-^{40}Ca isotope pair, but was not limited by exchange reaction kinetics (4).

The size of the isotope effect with 18-crown-6 was known to be highly dependent on solvent composition (4), so the authors considered the possibility of improving the isotope effect by modifying the composition of the fluid phase. Work with methanol and chloroform mixtures over a range of 0 to 50 volume percent chloroform had shown that a 70/30 mixture yielded the largest isotope effect (4).

The use of dimethylsulfoxide (DMSO) in lithium-macrocycle liquid-liquid exchange systems was reported by Nishizawa et. al. (5). In these systems, the lithium isotope effect was unchanged when DMSO was added; however, the lithium distribution was changed.

The work described below investigated the effect of adding DMSO to the fluid phase of the calcium-crown exchange system. The

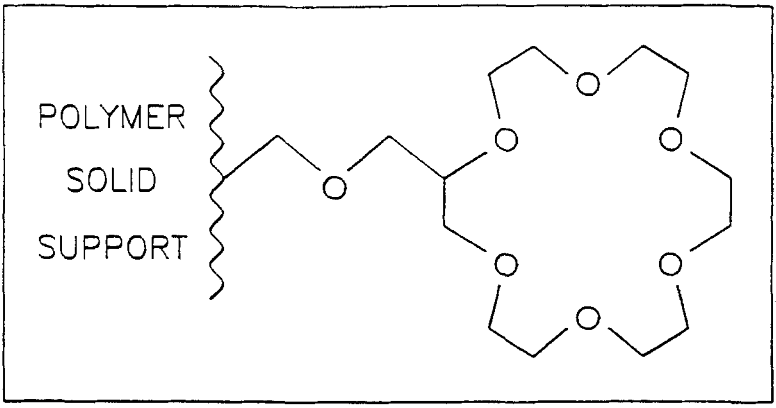

FIGURE 1. Structure of the ligand-tether combination. Synthesis of the ligand-tether and preparation of the packing was done by R. A. Bartsch, Texas Tech University (6).

work was directed specifically to calcium isotope exchange with polymer-bound 18-crown-6. The primary purpose was to determine the influence of DMSO on the fundamental properties of the exchange including

- The separation coefficient of the isotope exchange reaction, and
- The binding constant of the calcium-crown complexation-decomplexation reaction.

EXPERIMENTAL

Column Description

Columns were jacketed glass, 0.65 cm in diameter and five cm long with adjustable endpieces to accommodate varying packing lengths and packing expansion. The packed lengths at the conclusion of the column runs are listed in Table 1. The quantity of packing for Runs 1-3 was 0.268 dry grams with an 18-crown-6 content of 2.08 mmole/dry gm.

The polymer-bound 18-crown-6 was prepared by R. A. Bartsch at Texas Tech University (6). Figure 1 shows the structure of the ligand-tether combination. The solid support was microporous, polystyrene, divinylbenzene with a nominal one percent crosslinking.

Column Operation

The breakthrough technique was used. Calcium chloride feed solution was pumped through the column until steady-state conditions were reached and no changes in either isotopic composition or effluent calcium concentration were occurring. The feed flow rate was 0.01 cc/min for all three runs. The composition of the feed solutions are shown in Table 2. The effluent sample size was 0.15cc.

After the completion of each run, the total calcium in each column was also recovered, and samples were prepared for mass ratio analyses. The mass ratios of these samples permitted an estimate of the void fraction in the columns. This ranged from 0.2 to 0.5 with an average of 0.3 (4). Table 1 shows column loadings, fractions of crown complexed, and HETP'S (Height Equivalent of a Theoretical Plate).

Sample Analysis

The samples were prepared as described previously (3). The samples containing DMSO were heated to >220 °C for 8 to 12 hours to remove DMSO. The samples were analyzed for calcium content by inductively coupled plasma spectroscopy (ICP) and for isotope ratios by thermal ionization mass spectrometry (TIMS). The mass spectrometer used in this work was a Finnigan MAT 261.

The same preparation procedure previously described (3) was performed by a laboratory robot. All samples were analyzed

TABLE 1. COLUMN PARAMETERS AND PERFORMANCE

Temperature = 20.0°C

Run No.	Column Length, cm	Column Loading, M[a]	Fraction Complexed[b]	HETP[c], mm
--[d]	4.3[e]	0.54	0.87	0.15
1	2.96	0.31	0.51	0.4
2	2.70	0.54	0.81	3.3[f]
3	2.80	0.56	0.87	1.1

[a] Calcium/Unit Volume of Column, both phases, moles/liter.
[b] Mmole Calcium (Solid phase)/ Mmole 18-Crown-6 in Packing.
[c] Height Equivalent of a Theoretical Plate, from Fenske Equation.
[d] Run #2, from Reference 4.
[e] This column contained 0.39 grams packing cf 0.268 for other Runs.
[f] Channeling.

including 40 to 90 samples for each column run. Mass ratios were also measured for the recovered calcium in order to estimate the void fraction in the columns (4).

Along with the enriched samples from the column, approximately 30 reference samples were analyzed. The calcium 40/44 ratio of the reference solution was 46.38 ± 0.01 (2σ).

RESULTS AND DISCUSSION

The purpose of this work was to ascertain the influence of DMSO on the two fundamental properties:

- The separation coefficient, and
- The binding constant for the complexation-decomplexation reaction of calcium with polymer-bound 18-crown-6.

These results are summarized in Table 1 along with the results from prior work on this system that with no DMSO.

Separation Coefficient

Isotope enrichment of calcium-44 proceeds according to the following chemical exchange reaction:

$$^{40}Ca^{2+}_{(fluid)} + {}^{44}CaL^{2+}_{(solid)} \rightleftharpoons {}^{44}Ca^{2+}_{(fluid)} + {}^{40}CaL^{2+}_{(solid)} \qquad (1)$$

where $L_{(solid)}$ represents the polymer-bound 18-crown-6. The heavy isotope, ^{44}Ca, is enriched in the fluid phase according to Reaction 1 and is enriched in the calcium samples taken at the front of the band. For Reaction 1 the separation coefficient, ϵ, is equal to K_{ex} - 1 where K_{ex} is the equilibrium constant for exchange Reaction 1.

The separation coefficients were calculated from the following expression:

$$\epsilon = \frac{\Sigma q_i (n_i - n_o)}{Q_s n_o (1 - n_o)} \qquad (2)$$

where n_i is the atom fraction of ^{44}Ca in the i^{th} fluid sample,

q_i is the total quantity of calcium in the i^{th} fluid sample, and

Q_s is the calcium capacity of the solid phase.

The separation coefficients were obtained from the summation of these values over the full range of enriched samples according to Equation 2. It should be noted that these coefficients are for the ^{44}Ca-^{40}Ca isotope pair.

The results shown in Table 2 show a significantly larger separation coefficient for crown systems containing DMSO than those that do not. The separation coefficient, ϵ, for the ^{44}Ca-^{40}Ca isotope pair increased from $\epsilon=0.0025\pm0.0002$ to $\epsilon=0.0035\pm0.0003$ when DMSO was added. This change in the isotope effect is most likely a consequence of the formation of a calcium solvate (complex) with DMSO in the fluid phase.

TABLE 2. SEPARATION COEFFICIENT, ε, AND LOG OF BINDING CONSTANT, K, FOR VARIOUS FLUID PHASE COMPOSITIONS

	Components Added To MeOH/$CHCl_3$[b]				
Run No.	$CaCl_2$, M	DMSO,%[c]	H_2O,%[c]	Binding Constant $\log_{10}K$	Separation Coefficient $\epsilon(^{44}Ca-^{40}Ca)$,95%CL
--[d]	0.086	0	0.5	1.8	0.0025 ± 0.0002[e]
1	0.077	5.0	0.5	1.1	0.0035 ± 0.0003
2	0.103	2.0	0.2	1.6	0.0035 ± 0.0003
3	0.098	0	0	1.8	0.0027 ± 0.0003

[a] Tether, $-CH_2OCH_2-$; ligand, 18-crown-6; 1% crosslinked polystyrene divinylbenzene solid support.

[b] Fluid phase stock solution consists of 70/30 methanol/chloroform by volume.

[c] Component added to fluid phase to obtain volume % shown.

[d] Run #2 from Reference 4.

[e] Separation coefficient is average of six determinations with the same solvent system but differing tethers; i.e., the separation coefficient is independent of tether structure.

Binding Constant

As can be seen in Table 2, the presence of DMSO in the fluid phase also has an influence on the stability of the calcium-crown complex. The heterogeneous complexation-decomplexation reaction of calcium with 18-crown-6 can be shown in its simplest form:

$$Ca^{2+}_{(fluid)} + L_{(solid)} \rightarrow CaL^{2+}_{(solid)} \qquad (3)$$

While each of the three species in Reaction 2 is solvated, the exact nature of the solvation is not known. Each species can solvate with four solvents: water, DMSO, methanol and chloroform. The number and type of solvating ligands for each species and their activities in Reaction 3 are not known.

It was nevertheless useful to obtain binding constants for Reaction 3. The concentrations of the species in Reaction 3 were known or calculated, and binding constants, K_{bind}, were calculated. $[Ca^{2+}]_{fluid}$ was accurately known from the fluid phase preparation, the crown content of the packing was known from elemental analysis, and $[CaL^{2+}]_{solid}$ was obtained by determining the difference between the measured total calcium capacity of the column and the total calcium in the fluid phase within the column. For that purpose, a void fraction of 0.3 was assumed (4). Calcium was assumed to be present on the solid phase only as the crown complex. With these observations and assumptions, the binding constants for Reaction 3 can be expressed:

$$K_{bind} = \frac{[CaL^{2+}]_{solid}}{[Ca^{2+}]_{fluid}[L]_{solid}} \qquad (4)$$

where the concentration of the uncomplexed ligand $[L]_{solid}$ is obtained by difference.

As can be seen in Table 2, the stability of the calcium complex decreases as the DMSO concentration increases. The reduction of $\log_{10}K_{bind}$ with increasing DMSO suggests that DMSO bonds more strongly with the calcium ions in the fluid phase than does the water (or methanol) of solvation in systems without DMSO. The molar concentration of 2% DMSO is 0.28<u>M</u>, approximately stoichiometric for fluid phase concentrations of tri-DMSO calcium.

Influence of DMSO

Reactions 1 and 3 are written in simplified form without indicating coordinating solvent species. The solvents, being part of the coordination sphere of the calcium ions, can be expected to influence both of the following:

o Complex stability (binding constant), and o The relative stabilities of the same chemical species with differing calcium isotopes (separation coefficient).

Since DMSO influences both of these, one can infer that DMSO is involved in the coordination of calcium ions in one or both of the calcium species in Reactions 1 and 3.

This inference is supported by reports in the literature. Franklin and Owen were the first to construct a ternary diagram for the DMSO-water-$CaCl_2$ system (7). This phase diagram was developed at 37°C. This work identified a compound with the composition, $CaCl_2 \bullet 3H_2O \bullet 3DMSO$. The 1:3 ratio of Ca:DMSO was obtained by both chemical and thermogravimetric techniques. The water content was obtained by difference. The relatively straightforward ternary diagram also was consistent with this composition.

Later, Felker and Kelmers constructed a ternary diagram for $CaCl_2$-DMSO-H_2O at 25°C (8). Their conclusion was that $CaCl_2$-DMSO-H_2O compounds may exist; however, specific compounds were not identified. Toktomatov et.al. isolated and identified the $CaCl_2 \bullet 3DMSO$ compound in phase studies of the $CaCl_2$-DMSO-hexamethylenetetramine (HMTA) ternary system (9). This work also was done at 25°C.

In all of the above phase diagram studies, the existence of a solid phase compound containing $CaCl_2$ and DMSO was confirmed or suggested as a possibility. Two of the three studies specifically identified the tri-DMSO compound, $CaCl_2 \bullet 3DMSO$. Since a solid calcium tri-DMSO compound exists, it seems plausible that such a compound (complex) could exist in the fluid phase.

An inspection of CPK (Corey-Pauling-Kolton) models shows that a Ca-Crown-3DMSO complex is highly unlikely due to space restrictions. The influence of DMSO on the equilibrium coefficients in Reaction 1 and Reaction 3 can be reasonably attributed to the likely formation of a tri-DMSO complex in the fluid phase.

SUMMARY AND CONCLUSIONS

The separation coefficient, ϵ (for the ^{44}Ca-^{40}Ca isotope pair), increased from 0.0025 to 0.0035 as a result of adding dimethylsulfoxide (DMSO) to the calcium-crown chemical exchange system. The separation coefficient remained the same at two levels of DMSO concentration.

The binding constant for the calcium-crown complexation-decomplexation reaction was reduced when DMSO was added. This was a natural consequence of calcium ions bonding more strongly when DMSO was in the fluid phase than when it was not.

The influence of DMSO on the separation coefficient and the binding constant for the complexation-decomplexation reaction can be reasonably attributed to the formation of the calcium tri-DMSO complex in the fluid phase.

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