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Calcium Isotope Separation by Chemical Exchange With Polymer-Bound Crown Compounds

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ABSTRACT

Chromatographic separation of calcium isotopes by chemical exchange with polymer-bound 18-crown-6 was investigated. The breakthrough technique of column chromatography was employed to determine the influence of solvent composition and ligand-tether structure on separation coefficients and heterogeneous calcium complex stability. The separation coefficient, ϵ, was found to be strongly dependent upon solvent composition. An ϵ of 0.0025 ± 0.0002 (95% C.L.) for the $^{44}Ca/^{40}Ca$ isotope pair was obtained with a 70/30 (by volume) methanol/chloroform solvent mixture at 20.0°C. Differences in the structure of the tether binding the crown ring to the polymer had no influence on ϵ at that solvent composition.

The stability of the calcium-crown complex was strongly dependent on the structure of the tether and moderately dependent on solvent composition. The equilibrium constant, K, for the heterogeneous complexation-decomplexation reaction varied over two orders of magnitude. The $\log_{10}K$ values ranged from a low of 0.41 to a high of 2.59 largely as a consequence of variations in tether structure. The highest stability was attained with the structure (polymer)-$(CH_2OCH_2)_5$-(18-crown-6) in the solvent mixture described above.

KEYWORDS: calcium isotope, chemical exchange, chromatography, crown, 18-crown-6, separation coefficient, separation factor, isotope effect, isotope separation

I. INTRODUCTION

The chromatographic enrichment of calcium isotopes with polymer-bound ligands proceeds according to the chemical exchange reaction:

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

where L represents the complexing ligand. Heumann and Schiefer investigated Reaction 1 with cryptand [2_B22] as the complexing ligand and found separation coefficients for the 40/44 isotope pair from 0.0026 to 0.0057 over a wide range of temperature[1]. These isotope effects were sufficiently large to be of practical interest.

In more recent work, the author examined Reaction 1 from the perspective of theoretical stage heights and the associated stage residence times[2]. This work also yielded a large separation coefficient, 0.0039 at 20.0°C, for polymer-bound cryptand [2_B22] exchange. It was concluded, however, that a probable reaction rate limitation precluded any application of this reaction.

Calcium chemical exchange with dicyclohexano 18-crown-6 in liquid-liquid extraction systems has been shown to exhibit large isotope effects[3]. Furthermore, calcium is known to possess rapid complexation-decomplexation reaction kinetics with 18-crown-6[4]. Thus, a study of Reaction 1 with polymer-bound 18-crown-6 was begun and some preliminary results reported[2].

The work following is a continuation of that preliminary work. The ligand 18-crown-6 is a weak complexing agent for calcium, therefore, experimental conditions which enhance the

complex stability must be found. The structure of the tether binding the crown to the polymer solid support was varied to determine its influence on complex stability. In addition, the influence of solvent composition on the separation coefficients and complex stability was examined.

II. EXPERIMENTAL

Polymer-bound crown compounds were not available commercially. Figure 1 shows the structures of the ligand tether combinations used. Column packings I[5], III, IV, V, and VI were acquired from Prof. R. A. Bartsch at Texas Tech University, and II was prepared at Mound Laboratory[6]. The crown content of each of the packings was determined by elemental analysis. The solid supports were obtained from 200 to 400 mesh chloromethylated (4.2 meq/g) polystyrene divinylbenzene from Fluka and Bio-Rad.

Column runs were performed in jacketed glass columns maintained at 20.0°C. Feed solutions consisted of methanol chloroform mixtures (listed later in this paper) to which 0.5% water and anhydrous calcium chloride were added. Calcium concentrations were: 0.110M (Runs 3,4,7), 0.103M (Runs 9,10,11), 0.100 M (Runs 5,8), 0.086M (Run 2), and 0.010M (Run 1). Additional details are available in the Report MLM-3654, available from NTIS.

The breakthrough technique of column chromatography was used for the determination of separation coefficients. It is useful to review this method in a general way, since detailed derivations often obscure the conceptual simplicity of the

method. In brief, a quantity of calcium chloride, in a uniformly mixed fluid phase, is passed through a column (initially totally free of calcium) until steady state is reached. Steady state has been reached when the concentration and isotopic composition of the column effluent equals that of the feed solution.

In the final state of the experiment the calcium from the initial feed solution has been divided into three categories according to isotopic composition. 1) Material with no isotope enrichment including the calcium in the fluid phase of the column and samples of effluent taken after steady state was reached. 2) The calcium retained on the solid phase, now at equilibrium with the fluid phase. This differs in isotopic composition from the fluid phase by exactly one equilibrium stage of separation. 3) The heavy isotopes transported out of the solid phase. These have been subsequently transported via the column fluid phase into the samples.

The total ^{44}Ca isotope transport, τ, is thus represented by the equation:

$$\tau=\Sigma q_i(n_i-n_o)=\epsilon Q_s n_o(1-n_o) \qquad (2)$$

where the summation term yields the excess of isotope collected in the samples, and the right-hand expression, the quantity of isotope removed from the solid phase at equilibrium. The quantities are, q_i, total Ca in the i^{th} sample, n_i and n_o the atom fractions of ^{44}Ca in the sample and feed, respectively, and Q_s the total Ca in the solid phase. The separation coefficient, ϵ, is thus an outcome of a simple material balance. The transient behavior of the column during the time interval between the

initial and final states of the column experiment is not relevant to its computation. It is necessary to verify that steady-state has been reached and that no further changes are occurring in the concentrations and isotopic compositions of the samples.

The total capacity of the column, Q_t, was obtained by recovering all calcium from the column at the completion of each breakthrough experiment. This recovery was accomplished by eluting methanol and methanol-water mixtures into a fraction collector until calcium could no longer be detected in the effluent samples.

The total calcium in the solid phase, Q_s, was obtained from the equation:

$$Q_s = Q_t - \nu V_{col} C_o \qquad (3)$$

where ν is void volume, V_{col} the column volume and C_o the feed concentration. Isotopic analyses of recovered material were sufficiently precise to confirm a void volume assumption of ν approximately equal to 0.3. That is, the isotope ratios of the recovered material were consistent with a weighted average of fluid phase isotope ratios and solid phase isotope ratios.

The calcium isotope ratio measurements were performed with a Finnegan MAT 261 thermal ionization mass spectrometer [2]. A thirteen sample turret was loaded with nine or ten experimental samples and three or four reference (feed) samples for each series. The external precision was less than 0.02%(2σ) on the $^{40}Ca/^{44}Ca$ ratio.

III. RESULTS

Figure 1 shows the various crown-tether combinations

investigated. The calcium breakthrough curve for ligand-tether combination V is shown as an example in Figure 2. The term q_i, mg Ca in each sample, from Equation 2 is plotted in this curve. Figure 3 shows the isotope enrichment profile for the same column run. The isotope ratio R_i ($^{40}Ca/^{44}Ca$) for each sample is plotted in that graph. Unless otherwise specified, all separation coefficients used in this report will refer to the calcium-40/44 isotope pair. Figure 3 illustrates the approach of R_i to the reference (feed) isotope ratio, R_o. This verifies that steady state has been reached, a necessary condition for the validity of the breakthrough technique.

For the computation of the separation coefficient, ϵ, Equation 2 is rearranged to yield:

$$\epsilon=(1/Q_s)\Sigma q_i[(R_o/R_i)-1] \qquad (4)$$

where Q_s and q_i are as previously defined. Equation 4 is an approximation which is valid for $n \ll 1$, and the small isotopic enrichments obtained in this work.

Table 1 summarizes the results for each of the column runs along with the tether structure and solvent composition. Run 7 was not completed due to a plugged column.

IV. DISCUSSION

The primary goal of this work was to define separation coefficients and calcium-crown complex stabilities in a chemical exchange system adaptable to displacement band chromatography. Chromatography columns characteristically exhibit the short

theoretical stage heights necessary for an enrichment process which requires a large number of stages.

The ligand 18-crown-6 does not form strong complexes with calcium in homogeneous solution [7,8]. Furthermore, it is well known that macrocycle complexes become less stable when functional groups are added or when the macrocycle is bound to a solid support. Thus, low calcium complex stability was expected to be an obstacle to developing a chromatographic crown system having utility for further development.

Both tether structure and fluid phase solvent composition were expected to be factors in complex stability. This study examined the influence of these factors on the calcium-crown complex stability. In addition, the influence of these factors on the separation coefficient and column loading were obtained.

1. Separation Coefficient

A goal of this work was to establish a chromatographic chemical exchange system with a separation coefficient of 0.002 or greater for the calcium 40/44 isotope pair. Table 1 lists the results of the column experiments. Runs 2, 3, 4, 8, 10 and 11 made with a fluid phase mixture of 70% methanol and 30% chloroform yielded an average separation coefficient of 0.0025 ± 0.0002 (95% C.L.).

Tether structure Five different tether structures were used in these six runs. The absence of variation in the separation coefficient indicated that tether structure had no influence on the separation coefficient at that solvent composition.

Solvent Composition The separation coefficient was found to be highly dependent on the composition of the solvent mixture. Figure 4 shows the separation coefficient as a function of solvent composition for each of the different column packings.

The dependence of the separation coefficient on solvent composition is consistent with chemical exchange theory. The isotope effect is primarily a consequence of the differences in isotopic vibrational frequency shifts occurring in the fluid phase solvated calcium species and in the solid phase complexed calcium species. Changes in the fluid phase composition change the coordination spheres of the solvated calcium species leading to differing isotope effects.

2. Complex Stability

The formation of the the calcium-crown complex proceeds according to the complexation-decomplexation reaction:

$$Ca^{2+}_{fluid} + L_{solid} \rightleftharpoons CaL^{2+}_{solid} \qquad (5)$$

where L represents the 18-crown-6 ligand. The 18-crown-6 complexes rather poorly with calcium. For example, complex formation from aqueous solution is negligible, thus the requirement for using organic solvents as fluid phases. The effective stability constant for this reaction determines the fraction of crown complexed in the column. For a system to have potential for practical applicability, a reasonably large fraction of the available crown must be complexed.

Figure 5 shows the influence of tether structure and solvent composition on the stability of the calcium crown complex. The equilibrium constant, K, was calculated for the heterogeneous

reaction shown in Equation 5. Several qualifying comments are necessary. It is assumed that all calcium ions in the solid phase are present as the calcium complex of the crown. That is, no calcium is adsorbed on the polymer surfaces nor is any calcium complexed with the tether rather than the crown ring. The lack of variation in the separation coefficient with different tethers tends to support the latter assumption, however, does not verify it. The concentration [L] of uncomplexed ligand in the solid phase is obtained by difference from the crown content less the calcium complexed in the solid. This value becomes highly uncertain as Equation 4 approaches completion ([L]→0). Thus the logK of 2.59 for Run 10 has a wide margin of error.

Tether Structure Tether effects can be examined by comparing the results in Column Runs 2, 3, 4, 7, 8, 10, and 11 in Table 1. In these experiments the solvent composition (70/30) and the ligand (18-crown-6) were held constant with only the tether structures changing.

In terms of fraction of crown complexed the tethers can be ranked from the best to the poorest showing ranking, tether, Run number and fraction complexed: 1. IV, Run 10, 0.99; 2. I, Run 2, 0.87; and V, Run 11, 0.86; 3. III, Run 8, 0.65; and, VI, Run 7, 0.63; and 4. II, Runs 3 and 4, 0.45. It is evident from this list that the presence of an oxygen in the tether near the crown is essential to complex stability. Somewhat less strongly, it can be concluded that long alkyl chains are detrimental to the complex stability.

An inspection of Corey, Pauling, and Kolton (CPK) molecular models shows that the tether oxygen near the crown is free to participate in the coordination of the calcium ion. Furthermore, with the IV, the two ether oxygens nearest to the complex can readily be oriented near the crown cavity while in the case of V, this orientation seems awkward and less likely to occur.

Solvent composition Figure 5 shows four pairs of runs in which the same tether-ligand combination was used with different solvent compositions. These are Column Packing I, Runs 1 and 2; Column Packing II, Runs 4 and 5; Column Packing III, Runs 8 and 9; and Column Packing VI, Runs 6 and 7. In every pair the measured fraction of crown complexed increased with increasing chloroform. The solvation environment for calcium ions in the fluid phase became less favorable with the presence of more chloroform. This increased the stability of the calcium-crown complex driving the complexation Reaction 5 towards completion.

The amount of available crown sites per unit volume of column is a property of the packing and is not influenced by the solvent composition.

3. Column Loading

It is desirable to obtain reasonably high column loadings as these are related to the separative power of a column. These are listed in Table 1 in units of moles Ca/liter of column and are referred to as average concentrations. Higher concentrations permit smaller diameter columns for a given separation.

There are two main factors which come to bear on the average concentrations attained. The first is the fraction of available

crown sites complexed with calcium, and the second, the amount of available crown sites per unit volume of column. The former has already been considered in the discussion on complex stability. A third factor of lesser importance is the fluid phase concentration. Fluid phase calcium concentrations have little impact on the overall average concentration since the volume occupied by the fluid phase is small and the fluid phase concentrations are generally much less that solid phase concentrations. Extremely low fluid phase concentrations may, however, adversly affect mass transfer rates.

The long tethers are bulky, however, and occupy space. As a consequence, the available crown sites on a given amount of polymer solid support are reduced with the longer tethers. For example, consider the three tether-ligand groups showing the largest fraction of crown complexed. I contained 2.0 mmoles crown per dry gram of packing, V contained 1.8, and IV contained 1.5. Expansion characteristics also change with tether differences with the longer tethers yielding less packing density after conditioning with the fluid phase.

From the standpoint of average concentration in the column, the shortest tether appears to have the greatest utility. A further consideration is that this tether-ligand combination is the least difficult to synthesize and bond to a solid support.

V. SUMMARY AND CONCLUSIONS

Calcium isotope separation by chemical exchange with polymer-bound 18-crown-6 was investigated. The breakthrough technique of column chromatography was used to determine

separation coefficients and calcium complex stability under conditions of varying tether structure and solvent compositions. The best chemical system found consisted of 18-crown-6 bound to a polymer support with a short tether, $-CH_2OCH_2-$, and a fluid phase of 70% methanol and 30% chloroform with 0.5% water. The separation coefficient for this system was 0.0025±0.0002 and the unit volume column capacity was 0.54 M calcium.

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Table 1 Separation coefficient, complex stability, and column loading for various tether structures and solvent compositions[a]

Run No.[b]	Tether Structure[c]	Solvent MeOH/$CHCl_3$[d]	Separation Coefficient[e]	Stability $Log_{10}K$	Column Loading[f]
1	I	100/0	0.0017	1.63	0.20
2	I	70/30	0.0025	1.83	0.54
3	II	70/30	0.0025	0.87	0.20
4	II	70/30	0.0026	0.79	0.16
5	II	50/50	0.0018	1.01	0.17
6	VI	100/0	0.0015	0.41	0.02
7	VI	70/30	ND	1.15	0.38
8	III	70/30	0.0027	1.20	0.24
9	III	80/20	0.0022	1.07	0.24
10	IV	70/30	0.0025	2.59	0.30
11	V	70/30	0.0024	1.72	0.26

[a]Temperature, 20.0°C, in jacketed columns. [b]Runs 1,2 and 3 from Reference 2. [c]Structures shown in Figure 1. [d]Plus 0.5% water; $CaCl_2$ anhydrous. [e]For the 40/44 isotope pair. Estimated error for each run: ±0.003 (95% CL). [f]Calcium per unit volume of column, M, both phases.

Figure 1. Structures of ligand-tether combinations in column packings. I is shown with polymer, II through V show tethers only. VI consists of cyclohexano 18-crown-6 with the same tether as I. Sources are listed in the text.

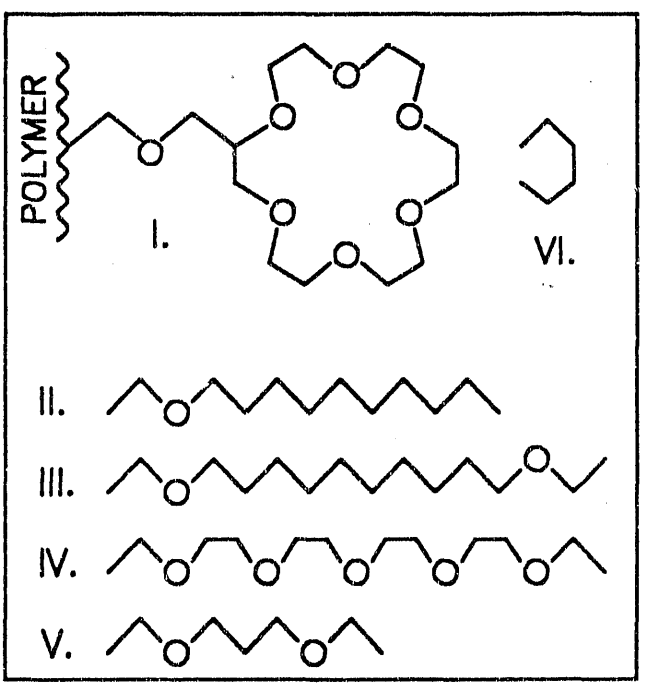

POLYMER
I.
VI.
II.
III.
IV.
V.

Figure 2. Breakthrough curve for Run 11 with column packing V. The solvent was 70/30 methanol/chloroform + 0.5% water by volume.

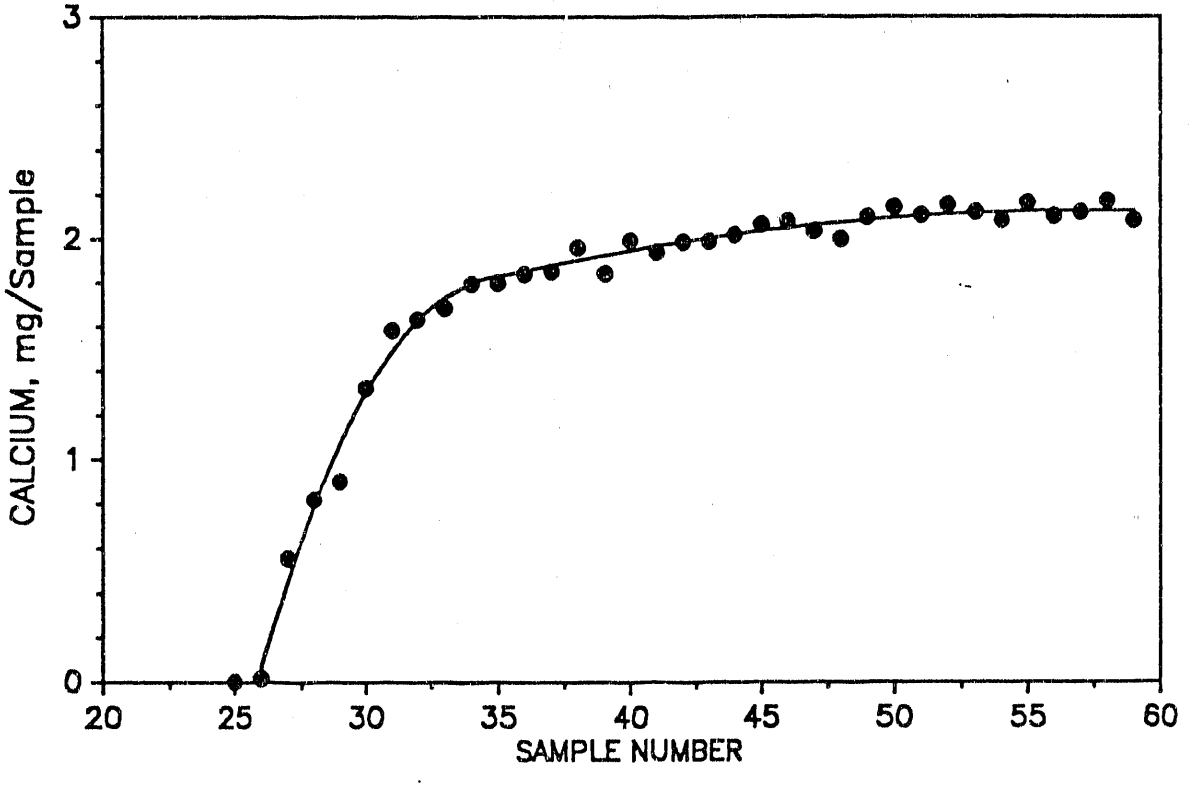

CALCIUM, mg/Sample
3
2
1
0
20
25
30
35
40
45
50
55
60
SAMPLE NUMBER

Figure 3. Calcium-44 isotope enrichment profile for Run 11 with column packing V. The separation coefficient was 0.0024.

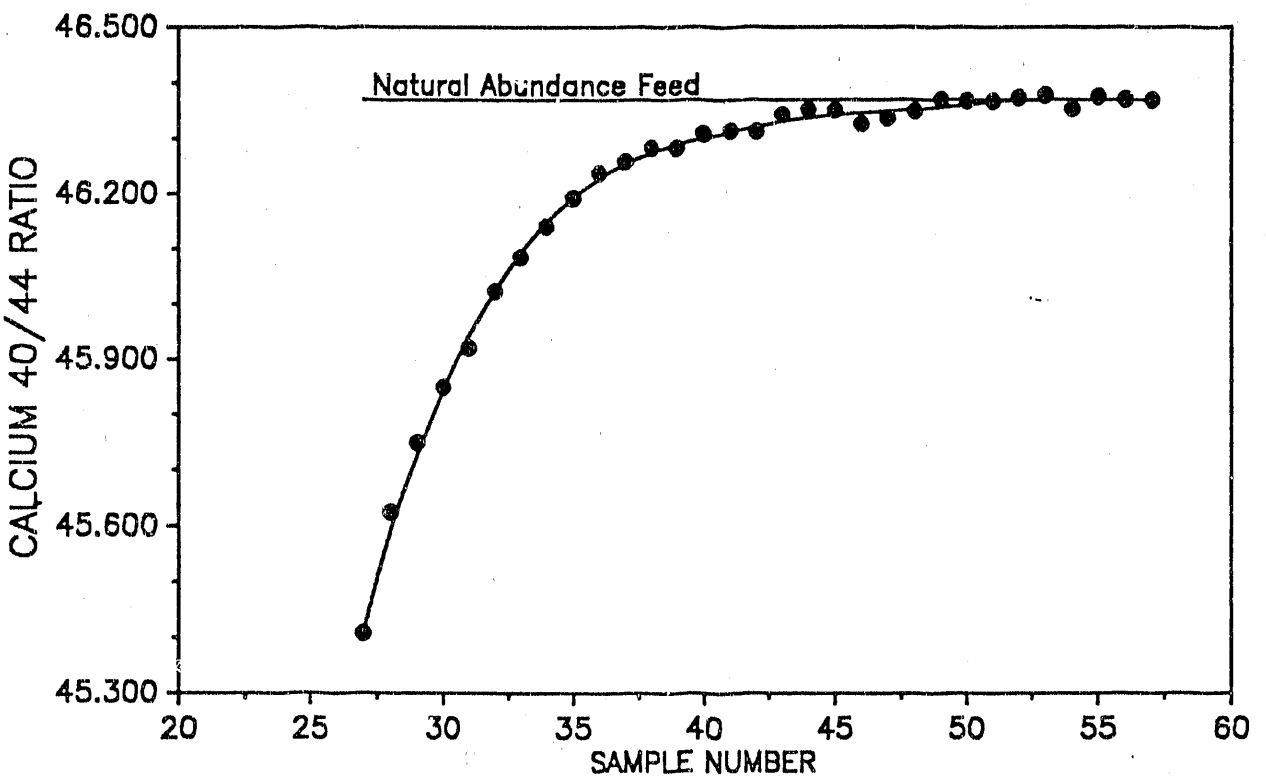

Natural Abundance Feed
46.500
46.200
45.900
45.600
45.300
CALCIUM 40/44 RATIO
20
25
30
35
40
45
50
55
60
SAMPLE NUMBER

Figure 4. Separation coefficient, ϵ, as a function of solvent composition. The line connects averages and points. At 30% chloroform, $\epsilon = 0.0025 \pm 0.0002 (2\sigma)$.

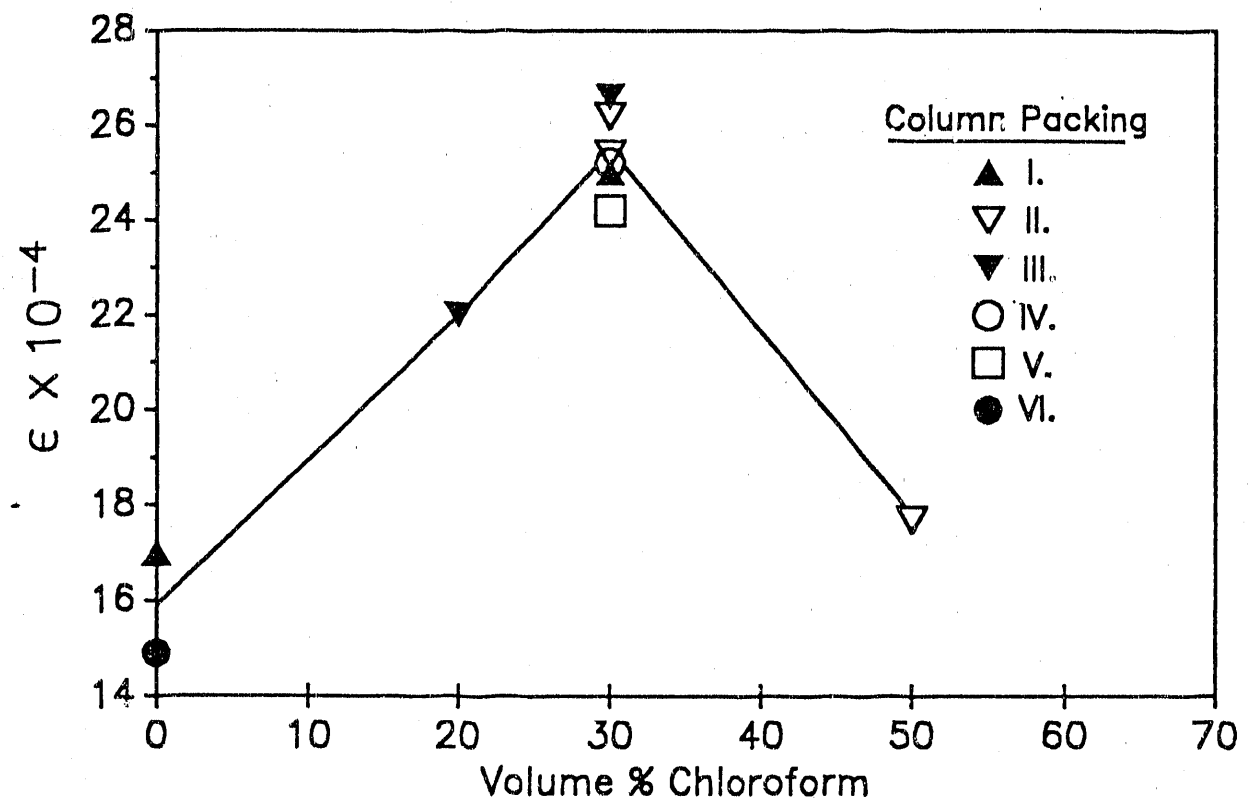
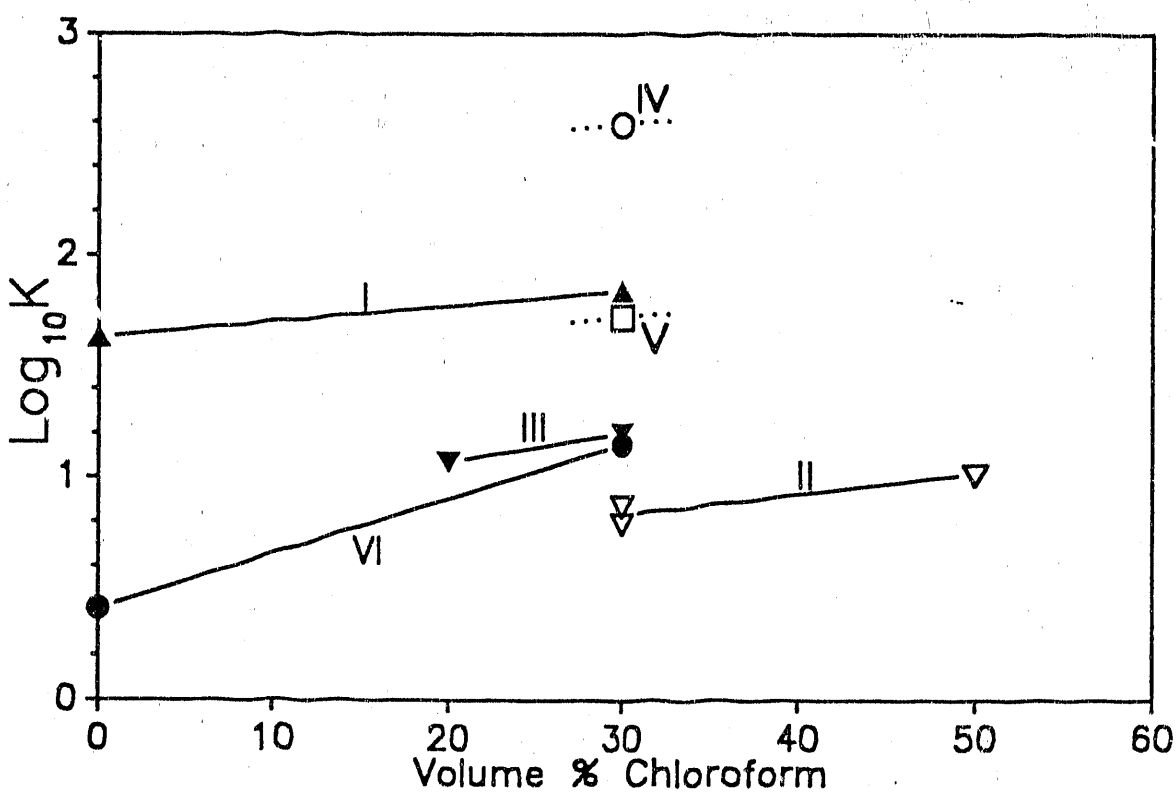

28
26
24
22
20
18
16
14
ε X 10−4
0
10
20
30
40
50
60
70
Volume % Chloroform
Column Packing
I.
II.
III.
IV.
V.
VI.

Figure 5. Influence of tether structure and solvent composition on calcium-crown complex stability. K is the equilibrium constant for the complexation-decomplexation reaction. Tether structures for packings I through VI are shown in Figure 1.


3
2
1
0
$Log_{10}K$
IV
I
V
III
II
VI
0
10
20
30
40
50
60
Volume % Chloroform

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