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COLUMN PHENOMENA IN THE GAS–LIQUID CHROMATOGRAPHY OF METAL β-DIKETONATES

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SUMMARY

Results of studies defining the partitioning and non-equilibrium phenomena observed when mixed-ligand complexes of the lanthanides are gas chromatographed are reported. An equation describing the retention volume of the mixed-ligand complexes is presented in which adsorption at the liquid and solid surfaces and solid–liquid interface are accounted for. Bulk liquid partitioning ratios and solid adsorption coefficients are evaluated. The nature of column loading and displacement is reported to be liquid phase dependent as well as dependent upon the complex itself.

INTRODUCTION

Since the initial report of the gas chromatography of metal β-diketonates in 1963[1], workers in the area have reported many non-ideal column phenomena. Frequent observations of column "loading" and the displacement[2-8] of previously studied complexes have been reported. The peak shape of the eluted species is commonly asymmetrical and the HETP realized is much lower than that found in studies of organic compounds of comparable volatility. This non-ideal column performance has been the limiting factor to the development of quantitative methods by gas–liquid chromatography (GLC). Quantitative methods for only the extremely volatile beryllium–TFA[9], inert chromium–TFA[10], and mixed-ligand complexes of uranium and thorium[11] and the lanthanides[12] having been successfully developed. The nature of the partitioning of metal chelates on GLC columns has been studied by VEENING AND HUBER[6] and SIECK[7]. They have reported the retention volume, V_{Rg}^{0}, to be a function of partitioning of the metal chelates with the liquid phase, KV_{L}, and a function of adsorption by the solid support, $k_{s}A_{s}$. UDEN AND JENKINS[8] have suggested

that displacement phenomena were also a result of interaction with the solid surface; however, precise experimental evidence was not presented to support this conclusion.

Earlier we reported[12] improved success in GLC of β-diketonates by varying liquid phase composition and percentages. This paper describes the nature of partitioning of mixed-ligand complexes of the lanthanides with various liquid phases and elucidates the nature of the non-ideal phenomena observed.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard Model 5756-B gas chromatograph equipped with a flame ionization detector (FID) was used for all column studies. The chromatograms were recorded with a Hewlett-Packard Model 7128-A strip chart recorder. The following instrumental operating conditions were used in the studies: columns were stainless steel, 20 × 0.25 in. O.D., temperature, 200°; helium carrier flow-rate, 50 ml/min; pressures, air, 33 p.s.i.g., hydrogen, 8 p.s.i.g.; temperatures, injection port, 280°, FID, 290°. Fluorescence data were obtained using an Aminco-Bowman spectrophotofluorimeter equipped with a Mosely X-Y recorder.

Reagents

Chromosorb W-HP, 100–120 mesh, Chromosorb P, 100–120 mesh, and silanized glass beads, 100–120 mesh, were used as solid supports throughout the studies. The liquid phases SE-30, QF-1, and Dexsil 300 GC were all obtained from Analabs, Inc.

The ligand 1,1,1,2,2,6,6,7,7,7-decafluoro-3,5-heptanedione (H(FHD)) was prepared in our laboratory as previously reported[12]. Di-n-butylsulfoxide (DBSO) was obtained from Aldrich Chemical Co. and was used after recrystallization from low-boiling petroleum ether. Rare earth oxides of 99.9% purity were prepared by ion-exchange chromatography at this laboratory. All other chemicals were reagent grade or better.

Stainless-steel columns used were prepared from laboratory stock stainless-steel tubing. Glass columns were prepared from Pyrex, borosilicate glass tubing.

GLC columns

The column packing was prepared by placing 5 g of dry solid support in a 2 × 10-in. cylindrical tube fitted with a glass frit. A solution of liquid phase in twice the wetting volume of the support, was poured into the tube and mixed with the support. The excess solute was drained from the support through a stopcock below the glass frit. Filtered air was then passed through the packing while heat was applied by infrared lamps.

All columns were washed with methylene chloride, acetone, and ethanol, and air-dried before packing. The dried column packing as prepared above, was then poured into the columns and compacted by agitation from a Burgess Vibro-graver.

The columns, with the exception of the Dexsil 300 GC columns, were conditioned at 50° below maximum operating temperature for the particular liquid phase, for 1 h without flow, and then 3–5 h with a helium flow of 50 ml/min. The Dexsil 300 GC columns were conditioned for 1 h at 250° without flow, then the temperature was

programmed to 350° at 4°/min and held at 350° for 5 h with a helium flow of 50 ml/min.

Identifications of species

Samples were collected, as eluted from the gas chromatograph, in glass collection traps in which a ball of glass wool had been placed. The collection traps were placed at the exit end of the column and air-cooled to room temperature. The collected samples were then washed from the trap with a solvent suitable for subsequent analysis.

Preparation of complexes

Mixed-ligand complexes of the lanthanides were prepared in cyclohexane solution by solvent extraction from rare earth chloride by the procedure of BURGETT AND FRITZ[12]. Equilibrium was established by shaking for 30 min on a Burrel wrist action shaker. After equilibration samples were withdrawn from the cyclohexane phase by syringe and injected into the gas chromatograph.

RESULTS AND DISCUSSION

Partitioning of metal–mixed-ligand complexes

The basic equation for partitioning in GLC has been developed through an extension of distribution theory for solute distribution between two phases in equilibrium, and can be written[13]:

$$V_{Rg}{}^0 = KV_L \tag{1}$$

where $V_{Rg}{}^0$ is the corrected retention volume per gram of packing, K is the partition coefficient for the solute in the liquid phase, and V_L is the volume of the liquid phase per gram of packing.

For years this equation was accepted as adequately defining the retention volume observed. Recently[14,15] other contributions such as adsorption at the solid surface and adsorption on the liquid surface, have been found to play an important part in determining retention volume. By including all terms known to be potential contributors to the retention of a solute on a GLC column, the resultant general equation would appear as follows:

$$V_{Rg}{}^0 = KV_L + k_a A_L + k_s A_s + k_0 V_0 \tag{2}$$

where KV_L represents the contribution to retention from partitioning of the solute between the gas and the liquid phase; $k_a A_L$ represents the contribution to retention from adsorption of solute on the surface of the liquid phase; $k_s A_s$ represents the contribution to retention from adsorption of the solute on the bare support; $k_0 V_0$ represents the contribution of solute interaction with the liquid phase either at the solid–liquid interface or at highly oriented layers or both. Which terms predominate is dependent on the system studied and the experimental conditions.

VEENING AND HUBER[6] have reported the partition ratio, k, to be a function of the phase ratio, q, for different chelates, as shown in the following equation

$$k = Kq \tag{3}$$

where K is the partition coefficient, and q is the phase ratio or ratio of the volume of the liquid phase to the gas volume of the column.

Experimentally the partition ratio can be easily obtained according to the following equation

$$k = \frac{(t_r - t_{r0})}{t_{r0}} \tag{4}$$

where t_r is the retention time of the solute in minutes, and t_{r0} is the retention time of an unretained solute such as air or methane in minutes.

The phase ratio is related to the weight of the liquid phase by a constant, (density of liquid phase $\times$ gas volume)$^{-1}$.

To be suitable for use in GLC determination of the lanthanides, the liquid phase must possess a high thermal stability. This requirement of high thermal stability eliminates all but a few of the currently available liquid phases. The phases used for this study were SE-30, a polysiloxane liquid with methyl substituents, QF-1, a polysiloxane liquid with methyl and 1,1,1-trifluoropropyl substituents, and Dexsil 300 GC, a carborane cage compound, cross linked by methyl substituted polysiloxane chains.

To determine the partition ratio, k, for the lanthanides with each phase a series of ten columns of 20 $\times$ 0.25 in. O.D. stainless steel was prepared. The packing used ranged from o to 25% w/w liquid phase. The partition ratio was determined using eqn. 4 and plotted *versus* the weight of liquid phase in the column. The mixed-ligand complex of terbium with H(FHD) and DBSO was selected for study for three reasons: (i) the complex fluoresces intensely, so eluents can be identified; (ii) terbium lies in the middle of the lanthanide series, so its column behavior should be intermediate between the extremely volatile and less volatile limits; and (iii) the mixed-ligand complex has been quantitatively chromatographed[12]. The GLC conditions of carrier flow, detector temperature, and column temperature were all held constant at 50 ml/min helium, 290° FID, and 200°, respectively. Methane was used to determine the value of t_{r0}.

Fig. 1 presents the partition ratio for the terbium complex as a function of the weight of liquid phase present for SE-30, QF-1, and Dexsil 300 GC columns. The linear variation of partition ratio with the amount of liquid phase indicates that gas–liquid partitioning is occurring between the mixed-ligand complexes and the liquid phases used. The similarity in partitioning observed with Dexsil 300 GC and SE-30 is a result of the similarity in polarity of the two phases.

The partitioning is greater with QF-1 than with either SE-30 or Dexsil 300 GC. This increased partitioning is a result of the increased polarity of QF-1. QF-1, a phase of intermediate polarity, would be expected to interact to a higher degree with the polar DBSO containing complex than would either of the non-polar phases SE-30 and Dexsil 300 GC.

All curves have a non-zero intercept, which terminates at the same value, that of the partition ratio observed with no liquid phase present. VEENING AND HUBER[6] have suggested that this observation indicates some of the complex is retained by the solid support used in the GLC column. If only gas–liquid partitioning were occurring, a zero intercept would be anticipated for these plots.

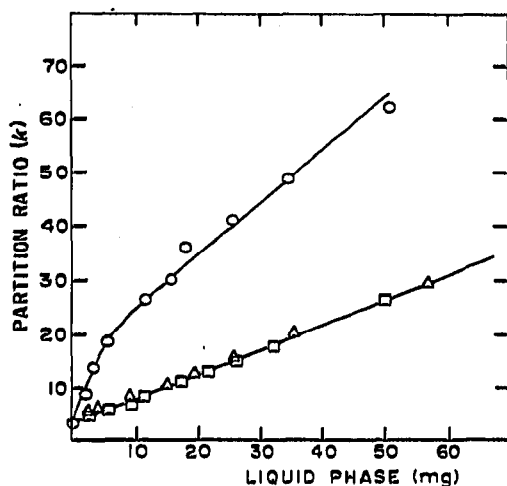To ascertain whether or not actual adsorption on the solid surface was occurring,

Fig. 1. Variation of partition ratio as a function of milligram amount liquid phase present at constant carrier flow and temperature. ○, QF-1; □, SE-30; △, Dexsil 300 GC.

two additional columns, both 20 × 0.25 in. stainless steel, were prepared. The first was packed with 100–120 mesh silanized glass beads and the second was packed with 100–120 mesh Chromosorb P. The silanized glass beads should be totally inert to adsorption and the Chromosorb consisting of ground fire brick, is a very active adsorbent. The conditions of flow and temperature were held constant at 50 ml/min helium and 200°, respectively.

Chromatograms were obtained for Tb(FHD)₃·2DBSO on both of these columns and the partition ratio, k, was calculated. The calculated ratios for all three uncoated supports are given in Table I. It is apparent from these data that it is not valid to

TABLE I

PARTITION RATIOS FOR Tb(FHD)₃·2DBSO ON VARIOUS UNCOATED SUPPORTS

Support		k
Chromosorb W-HP	100–120 mesh	3.5
Silanized glass beads	100–120 mesh	14.4
Chromosorb P	100–120 mesh	17.5

assume that a non-zero intercept for a k vs. phase(mg) plot indicates the total extent of solid surface partitioning. If this assumption were valid the k value for the glass beads should be the lowest. The high k value for the glass beads is probably a result of the more efficient packing realized by the glass beads. This tight packing creates a distillation column of a great number of theoretical plates. The boiling point difference between the complex and methane causes an apparent increase in partitioning of the chelate.

The difference in partition ratio for the Chromosorb P and Chromosorb W-HP is a result of increased adsorption on the Chromosorb P, since both of these supports should pack similarly. The partitioning observed with the Chromosorb W-HP is not totally a result of solid adsorption. Volatility differences between the chelates and

the unretained solute may increase the observed value. The k observed is the maximum value possible as a result of adsorption on the solid support. To obtain accurate assignment of partitioning caused by solid adsorption, a non-retained solute of similar volatility to the compound of interest must be used. This corrects for apparent partitioning caused by volatility differences.

The plot for partitioning on QF-1 would extrapolate to a higher k value than that observed on bare support. This additional contribution to the partitioning is a result of adsorption on the liquid surface. The point of inflection for this plot occurs at approx. 5 mg of QF-1, which for this column corresponds to a 2% coated column. CRAIG[16] has determined that at this point the surface of the solid support is completely covered. Evidently at loadings less than 2% the effect of solid surface adsorption begins to predominate at the loss of bulk liquid partitioning and liquid surface adsorption.

For QF-1 columns at least three phenomena must be contributing to the retention volume: (i) bulk partitioning with the liquid phase, KV_L; (ii) adsorption on the solid support, k_sA_s; and (iii) adsorption on the surface of the liquid phase, k_aA_L. For the SE-30 and Dexsil 300 GC columns the net retention volume of the mixed-ligand complexes is apparently a function only of the partitioning behavior of the complex with the liquid phase, KV_L, and adsorption on the solid support, k_sA_s.

It is also possible that interaction with the bulk liquid by complexation or other forms of association may make an appreciable contribution to the retention observed when QF-1 is used as the liquid phase. This type of interaction is likely to occur when polar liquid phases are used and polar solutes chromatographed. Experimentally this results in chromatographic peaks which have sharp leading edges with long tailing edges[17]. As shown in Fig. 2, this peak asymmetry is observed when QF-1 columns are used but not when Dexsil 300 GC columns are used. Other non-equilibrium phenomena such as loading of coordination sites on the column, displacement of previously studied complexes and elution of complexes containing liquid phase should be observed if this association is occurring. Such phenomena have been observed and will be discussed in the following section.

Loading, displacement and other non-ideal column behavior of metal–mixed-ligand complexes

With the exception of chromium and beryllium, the quality of GLC reported for metal diketonates is poorer than that of organic compounds of comparable volatility. GLC peak shapes obtained are often asymmetric with many anomalous shoulders and other extraneous peaks, and evidence of interaction with the column packing is often apparent.

One of the most frequently reported observations in the study of metal diketonates has been the requirement of injections of a particular diketonate to "load" the column before peaks of consistent size and shape appear, indicating that adsorption sites are being deactivated[2-8,10]. The situation becomes more complicated for mixtures of metal chelates, where a sequence of adsorption, displacements and possibly further interaction and breakdown is involved.

To determine which columns would be most suitable for GLC of mixed-ligand complexes, nine 20 × 0.25-in. stainless-steel columns of Dexsil 300 GC, SE-30, and QF-1 were prepared in the phase range of 0.0–25% w/w. By maintaining the flow-
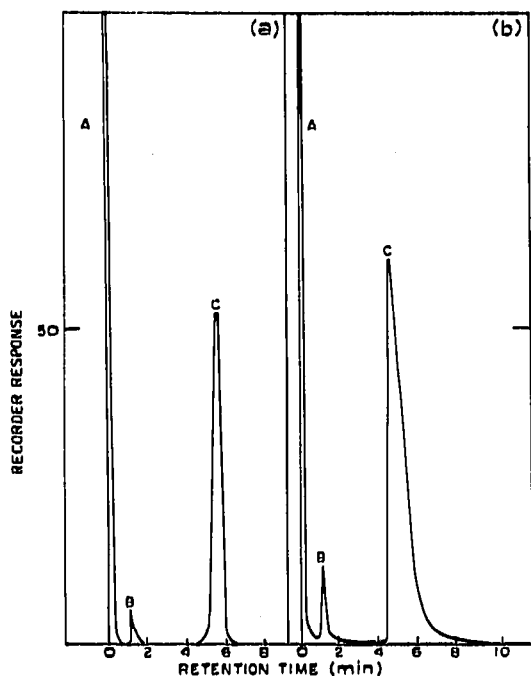
Fig. 2. Chromatograms of Tb(FHD)$_3$·2DBSO. 20 × 1/4 in. column, temperature 200°; liquid phase (a) 23.5% Dexsil, (b) 8.20% QF-1. A = cyclohexane-H(FHD), B = DBSO, C = Tb(FHD)$_3$·2DBSO.

rate and all other parameters constant and monitoring the precise history of the columns, the "loading" of each column was determined. Small sample volumes, 0.2 µl or less, of 0.01 M Tb(FHD)$_3$·2DBSO were injected into the chromatograph and elution of the chelates was determined by FID response. Assuming that the loading is additive, the amount of complex required before elution occurred was determined and plotted *versus* the weight of liquid phase (mg) present. In this manner the effect of the type and amount of liquid phase on the "loading" could easily be evaluated. The results of this experiment are shown in Fig. 3. For the liquid phases QF-1 and SE-30 the loading increases as the amount of liquid phase increases. The Dexsil 300 GC liquid phase apparently has the least loading of all phases. The loading for the Dexsil 300 GC columns is nearly constant with that observed with only solid support present. All of the curves extrapolate to the loading observed with no liquid phase present.

Previous workers[6,7] have attributed the loading to adsorption on active sites on the solid support. If this were the case the loading should be constant or diminish as the surface is covered by the liquid phase. This is not observed, except with the Dexsil 300 GC columns, therefore another mechanism must be proposed.

The loading may be occurring by non-equilibrium association or complexation with the liquid phase. As shown in Fig. 3, the loading is highest with the polar liquid phase, QF-1. The polarity of the liquid phase should enhance association with the polar complexes. If the association occurs within the liquid phase, an increase in

loading should be found as the amount of liquid phase increases. With the columns containing QF-I an increase of this type is observed.

The liquid phase SE-30 also possesses an appreciable loading. This loading is less than that observed when QF-I columns were studied. The decrease in loading is a result of a decrease in polarity of the liquid phase. The less polar phase would be expected to interact less strongly with a polar solute. The loading does increase as the amount of SE-30 in the column increases. As with the QF-I columns the increase indicates association or complexation with the liquid phase. Increased polarity enhances this interaction as does increased liquid phase thickness. UDEN AND JENKINS[8] have reported adsorption with polar liquid phases even on Teflon supports. In certain cases with polar phases they were unable to achieve elution of any chelates.
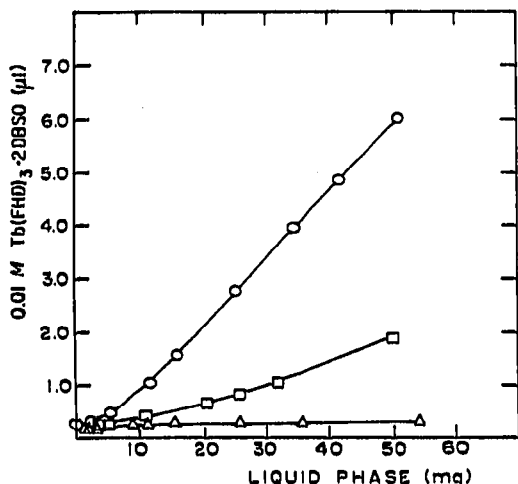

Fig. 3. Loading of columns with the mixed-ligand complex of $Tb(FHD)_3 \cdot 2DBSO$ as a function of milligram amount liquid phase present. ○, QF-I; □, SE-30; △, Dexsil 300 GC.

Dexsil 300 GC is both structurally similar, with the exception of the *m*-dicarboclovododecaborane cage units, and equal in polarity with SE-30. On this basis the loading should be similar. As shown in Fig. 3 the loading on Dexsil 300 GC does not increase as the amount of liquid phase increases. The loading remains constant at the level observed for bare Chromosorb W-HP. Evidently the carborane cages either offer steric interference to the interaction with the liquid phase or affect the manner in which the liquid phase is laid down on the support in such a way as to prevent association with highly oriented layers.

The solid support also makes a contribution to the loading. Evidence for solid support interaction is the constant loading of the Dexsil 300 GC columns. Furthermore, experiments with columns containing uncoated glass beads gave no indication of column loading. As the amount of liquid phase completely covers the solid support the active sites on the support should be covered and thereby be prevented from interaction. KELLER AND STEWART[18], however, have determined that even at 30% liquid phase the solute theoretically has time to reach the solid surface. Since the

solute can reach the surface under the chromatographic conditions described, interaction and loading at this surface can occur.

Apparently the loading is a multiple process which depends on the solid support, the polarity and structure of the liquid phase, and the nature of the complex.

Displacement of previously determined complexes by other metal complexes has also been observed. Columns containing QF-1 and SE-30 were found to exhibit this phenomenon. The displacement of europium by terbium could be observed by monitoring the apparent fluorescence of trappings from a column loaded with europium. The apparent fluorescence spectra for samples of Tb(FHD)$_3$·2DBSO collected as eluted from the chromatographed column are shown in Fig. 4. These

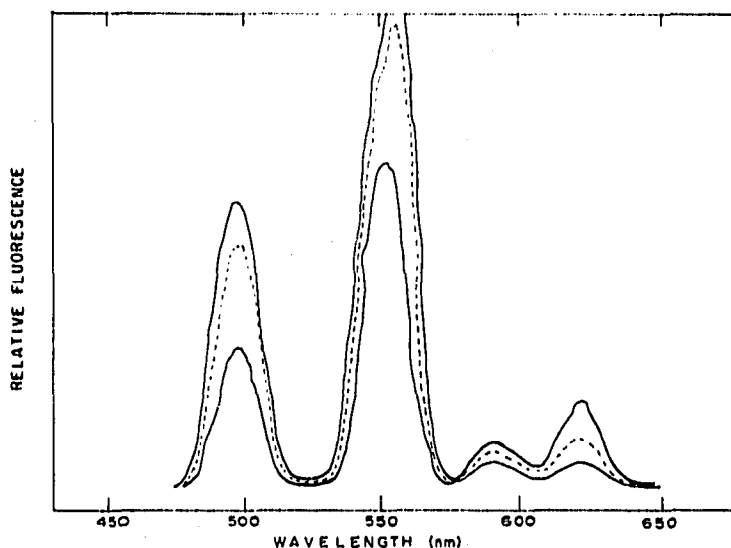Fig. 4. The apparent fluorescence spectra for displacement of Eu(FHD)$_3$·2DBSO by Tb(FHD)$_3$·2DBSO taken from trappings of column eluents. Excitation at 335 nm.

samples were chromatographed after several determinations of Eu(FHD)$_3$·2DBSO on the SE-30 column. The chelate exchange is obvious as the intensity of the fluorescence decreases. This exchange is quantitative as shown in Fig. 5. When the displacement behavior is observed chromatographically, the peaks have the same retention times as the individual complexes. The constant retention time is explained if a uniform loading of the initial chelate occurs throughout the column. As the second chelate starts through the column some of the previously loaded chelate is displaced. This displacement begins at the inport end of the column, then both complexes move down the column and are partitioned. Eventually all of the previously loaded complex is displaced (after several injections) and the column performs quantitatively for the new complex. This displacement interaction is particularly bad when polar liquid phases are used and has been observed even with Teflon solid supports[8].

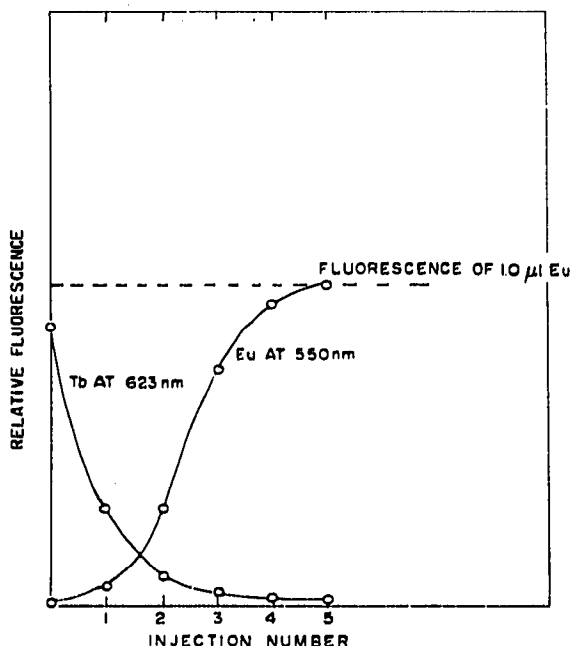Colums packed with Dexsil 300 GC were not found to exhibit this displacement

Fig. 5. Quantitative displacement of Tb(FHD)₃·2DBSO by Eu(FHD)₃·2DBSO on 5.0% SE-30 column.

phenomenon. This suggests that the displacement is related to the loading occurring on and/or in the liquid phase and not the loading on the solid surface.

The interaction with the solid surface has been reported to be a result of active hydroxyl groups present in the support material. UDEN AND JENKINS[8] suggested silanizing the solid support to eliminate these active hydroxyl groups. To assess the value of this technique, four 4 ft. × 0.25 in. glass columns were prepared in various states of silanization. These columns are listed in Table II.

TABLE II

GLC COLUMNS USED TO DETERMINE THE EFFECT OF SILANIZATION

No.	Column	Packing
1	Glass	5.0% SE-30 on Chromosorb W
2	Silanized glass	5.0% SE-30 on Chromosorb W
3	Silanized glass	5.0% SE-30 on silanized Chromosorb W
4	Glass	5.0% SE-30 on silanized Chromosorb W

Column 1 was used as a control column and demonstrated the loading and displacements discussed above. All columns which had been silanized demonstrated unsatisfactory chromatographic behavior. Column 3 showed the greatest loading and displacement phenomena of all the columns studied. Column 4 also showed extensive loading. Chromatograms obtained when columns 3 and 4 were used contained many spurious peaks, and the retention times of the complexes were observed

to decrease after several days of use. Apparently the silanization of columns and/or column packing material produces a detrimental effect on the elution of mixed-ligand complexes of the lanthanides and should not be done. This decrease in column performance on silanization suggests that the interactions may be occurring with the silicone polymers themselves.
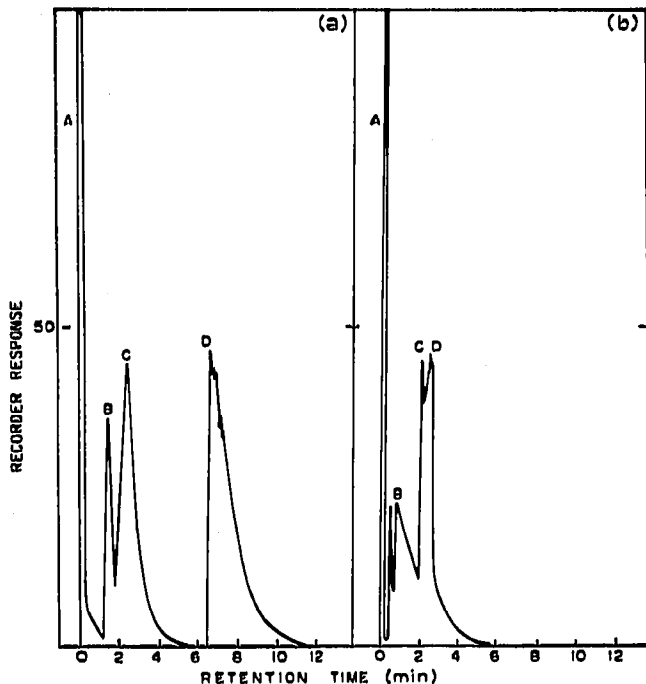

Fig. 6. Spurious peaks and shoulders observed with 20 × ¼ in. column, temperatures 200° (column) isothermal and 290° (FID). Liquid phase (a) 6.40% QF-1, (b) 5.09% SE-30. A = cyclohexane-H(FHD), B = DBSO, C = unknown, D = Tb(FHD)₃·2DBSO.

The last phenomenon observed is that of spurious peaks and shoulders. This phenomenon was noted in the studies utilizing QF-1 and SE-30 and is shown in Fig. 6. Qualitative identification, by eye observation, confirmed the presence of lanthanide in the extraneous peaks (the flame in the FID burned red, the characteristic color of the diketonate). Attempts at fluorescence analysis of trappings of the peaks failed to confirm the presence of complex. It is possible that some chelate decomposition or ligand-exchange is occurring in the bulk liquid. If this were the case injections of H(FHD) and DBSO, either singly or mixed, immediately following elution of chelates, should result in reformation of the complex and subsequent elution. When these experiments were tried no elution of complex was observed. UDEN et al.[10] also encountered this problem and successfully utilized mass spectral analysis to identify the peak composition for iron–TFA complexes. They report the composition to be the same as the injected chelate with the exception of traces of SE-30 bleed. Other workers have reported this type of interaction with gallium– and indium–TFA complexes[20].

These results show that when QF-1 and SE-30 are used as the liquid phase for metal GLC, care must be taken before retention times are reported. Particularly the history and age of the columns should be known as older columns may have less liquid phase.

No spurious peaks were observed in studies utilizing Dexsil 300 GC as liquid phase. Apparently the nature of this interaction is also liquid phase dependent and not solid surface controlled.

These non-equilibrium interactions have not been reported for the totally inert chromium complex. It is possible that the lack of interaction is a result of the inertness of the complex; since an inert complex would not be expected to associate with the liquid phase. If other inert complexes were prepared they too should be void of these interactions.

CONCLUSION

The retention behavior observed with mixed-ligand chelates includes contributions from partitioning on the solid surface, and with the bulk liquid. When polar liquid phases such as QF-1 are used additional contributions to the retention volume from liquid surface adsorption, complexation in the bulk liquid, and/or association in highly oriented liquid phase layers cannot be ignored.

Evidence has been presented which indicates column loading is a sum of solid support adsorption and association or complexation in the liquid phase. All other interactions are liquid phase dependent. These non-ideal phenomena are observed to a lesser extent when Dexsil 300 GC is used as a liquid phase. For this reason Dexsil 300 GC should be used for studies with mixed-ligand systems. The value of preparing inert complexes cannot be minimized. By elimination of possible coordination sites, specifically by the use of mixed-ligand complexes, non-equilibrium interaction is diminished.

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