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## CORRELATION ANALYSIS IN LIQUID CHROMATOGRAPHY OF METAL CHELATES

### I. ONE-DIMENSIONAL RETENTION-STRUCTURE MODELS IN REVERSED-PHASE THIN-LAYER CHROMATOGRAPHY

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#### SUMMARY

The predictive abilities of some parameters describing the effect of the structure of metal chelates on their chromatographic properties in reversed-phase thin-layer chromatography are compared. The applicability of corresponding one-dimensional equations for an *a priori* estimation of retention parameters, for optimization of the chelating reagent and for studying the mechanism of the interphase distribution of metal chelates is demonstrated. The dependences of the capacity factors on molecular structure parameters (distribution constant, stability constant, molecular connectivity index) are shown to possess the highest correlation factors. The necessity for the development of a multi-parametric model for describing the dependence of the chromatographic properties of chelates on their structure and the chromatographic experimental conditions is substantiated.

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#### INTRODUCTION

Metal chelates represent an important analytical form of metals in high-performance liquid chromatography<sup>1</sup>. The problems of forecasting the chromatographic behaviour of chelates at the quantitative level and the choice of the optimum chelating reagents for the selective separation of metals are of considerable interest. The solutions to these problems can be based on correlation equations relating the retention parameters with structural characteristics of metal chelates and applicable to other types of compounds. This paper assesses the applicability of one-dimensional dependences of such a type for the description of the chromatographic properties of metal chelates in reversed-phase thin-layer chromatography (TLC).

#### EXPERIMENTAL

##### *Chelates*

Metal dialkyldithiophosphates were prepared by extraction of metals with chloroform solutions of potassium dialkyldithiophosphates or by metal-exchange

extraction from nickel or zinc dialkyldithiophosphate and aqueous solutions of metal salts<sup>2</sup>. Metal diethyldithiocarbamates and di-*n*-propyldithiophosphinates were synthesized by mixing aqueous solutions of metal salts with sodium diethyldithiocarbamate and ammonium dipropyldithiophosphate, respectively.

#### *Chromatographic conditions*

The retention parameters were determined by TLC using precoated high-performance TLC plates with octylsilylated silica gel F<sub>254</sub> obtained from E. Merck (Darmstadt, F.R.G.). For higher reproducibility of  $R_F$  values the experiments were carried out at constant temperature ( $25 \pm 0.25^\circ\text{C}$ ) with presaturation of the sorbent layer by mobile phase vapour.

#### *Structural parameters*

The chelate distribution constants ( $K_D$ ) were calculated based on two-phase stability constants<sup>3</sup> and stability constants in water medium ( $\beta_n$ ). The  $\beta_n$  values, needed for calculation and correlation, were obtained from the linear dependence of  $\log \beta_n$  in aqueous-organic solutions<sup>4</sup> on the reciprocal of the dielectric constant<sup>5</sup>. To take into account the influence of the medium, the formalism of non-specific solvation parameters,  $IS^*$ , was used<sup>6</sup>. The  $IS^*$  values for water-organic mixtures were calculated from the tabulated values for individual solvents<sup>7</sup>.

The first-order connectivity indices ( $\chi$ ) for metal chelates were calculated according to Bondi<sup>8</sup>. The values of  $\delta$  (a formal parameter which takes into account the size of atom) for sulphur and phosphorus atoms, necessary for calculations, were taken from the same paper<sup>8</sup>. There is no information on any method for estimating  $\delta$  for metal atoms. Therefore, these parameters were calculated by applying the same logical approach, taking account of the variation of configuration of the outer electron shell of atoms during the formation of bonds with ligand donor atoms, by the following equation:

$$\delta(M) = \frac{Z^V - h}{Z + Z_d - Z^V(M) - 1}$$

where  $Z$  is the atomic number of the metal atom,  $Z^V$  is the total number of electrons participating in the formation of metal-ligand bonds,  $Z^V(M)$  is the number of electrons belonging to the metal atom itself,  $Z_d$  is the number of vacant  $d$ -orbitals of the metal atom and  $h$  is the number of bonded hydrogen atoms ( $h = 0$  for metals). Calculated  $\delta(M)$  and  $\chi(M)$  values are presented in Table I.

The molar volumes ( $V_m$ ) were calculated from functional group increments and Van der Waals radii of atoms<sup>9</sup>.

The induction ( $\sigma^*$ ) and steric ( $E_s$ ) constants were calculated from fragmental data<sup>10</sup> according to the additivity principle or reference values were used<sup>11</sup>. The hydrophobic constants ( $\pi$ ) and fragmental hydrophobic constants ( $f$ ) were taken from refs. 12 and 13.

The effective charges on metal atoms were estimated from the electronegativity of metal ( $\rho_M$ ) and donor atoms by using the principle of equalization of electronegativities<sup>14</sup>. The orbital electronegativity values (Klopman parameters,  $E_n$ ) were taken from the literature<sup>15</sup>. The ratios of  $\rho_M$  to metal ion radius were calculated from

TABLE I

 $\delta$  AND  $\chi$  VALUES FOR METAL ATOMS

<i>Metal</i>	$\delta$	$\chi$	<i>Metal</i>	$\delta$	$\chi$	<i>Metal</i>	$\delta$	$\chi$
Cd	0.178	10.05	Mn	0.320	7.49	Pd	0.186	9.83
Cu	0.320	7.49	Ni	0.320	7.49	Pt	0.105	13.08
Hg	0.104	13.15	Pb	0.107	12.96	Zn	0.296	7.79

reference data<sup>14</sup>. The metal increments ( $\Delta_M$ ) were calculated as the difference between the  $K_D$  values of the chelates and the chelating reagent.

## RESULTS AND DISCUSSION

Our objective is to compare the heuristic properties of as large a number of structural parameters as possible. In principle, to describe the effect of ligand structure one can use all the parameters which are applicable for organic compounds: the Hansch<sup>12</sup> and Rekker<sup>13</sup> constants, the number of carbon atoms<sup>16</sup>, the molecular connectivity indices<sup>8</sup>, etc. A more complicated situation arises when the influence of the nature of the metal and the structure of the chelate molecule as a whole have to be taken into account. For this purpose a knowledge of some special aspects of coordination chemistry is necessary.

### *Distribution constants*

The application of  $K_D$  values for the determination of the chromatographic properties of metal chelates (and of other compounds) is based on the idea that the intermolecular interactions in chromatographic systems and in systems of two immiscible liquid phases are similar<sup>17</sup>. The water-*n*-octanol system is usually considered as the optimum liquid-liquid system simulating the distribution of substances between a water-organic mobile phase and an alkyl-modified sorbent<sup>18</sup>. The method we applied for the calculation of distribution constants in various media allows the manipulation of the  $K_D$  values of chelates in an octanol-water-organic system of the same composition as the mobile phase. This approach makes the appropriate calculation of retention parameters more realistic.

Fig. 1 shows the dependences of  $\log k'$  values of metal chelates on the liquid-liquid distribution constants ( $r = 0.85-0.90$ ). These dependences satisfy the linearity hypothesis (according to the  $F$ -criterion at  $\alpha = 0.05$ ) although, in general, the correlation between chromatographic and extraction parameters was worse than expected. The reasons may be as follows: (i) the absence of reliable distribution constant data; (ii) the limited nature of the approach to their evaluation based on the principle of a linear free energy relation by using  $IS^*$  values<sup>6</sup>; (iii) the convention that the alkyl-modified sorbent surface is simulated by the voluminous octanol phase (according to our calculations the adsorption of metal chelates takes place without their penetration into the volume of the surface layer).

Nevertheless, the distribution constants can serve well for the determination of retention parameters, especially if one takes into account, in addition, a factor such as

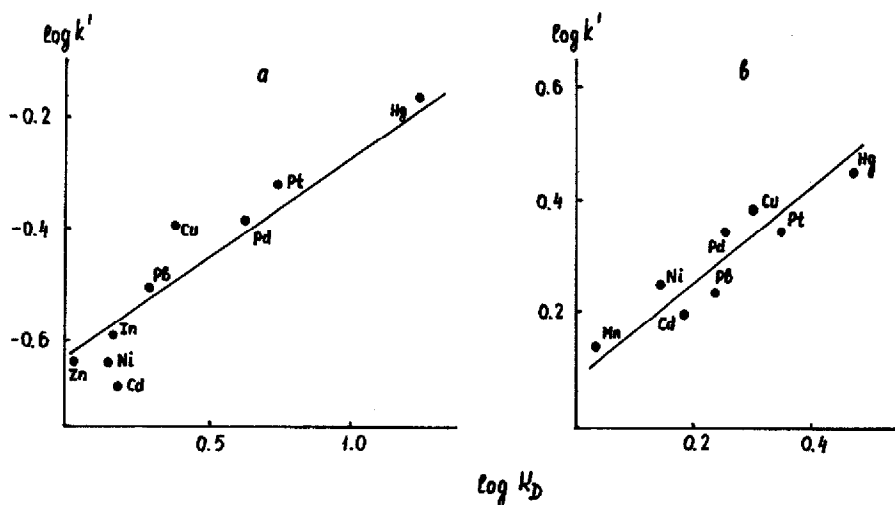


Fig. 1. Dependences of the retention parameters of (a) metal diethyldithiophosphates and (b) diethyldithiocarbamates on distribution constants. (a) Dioxane-water (80:20); (b) acetonitrile-water (80:20).

the differences between the donor-acceptor properties of an organic mobile phase modifier and the water phase of the extraction system by introducing some correction factors<sup>19</sup>.

#### Stability constants

According to modern ideas<sup>1</sup>, the character of chelate retention on non-polar sorbents from polar eluents is determined to a great extent by the specific intermolecular interactions of ligand donor (and other electronegative) atoms with electron-acceptor groups and atoms of the mobile phase components. On the other hand, in sulphur-containing chelates the metal-ligand bonds have essentially covalent character. As a result, owing to easy polarizability of soft ligands, the electron density is shifted into the interatomic region. The more stable the chelate, the stronger is the electron density shift to the central atom and, hence, the lower is the effective charge on donor atoms and the energy of corresponding specific interactions. In other words, more stable complexes should be less mobile than less stable complexes. The correlation between capacity factors and stability constants is just of this nature (Fig. 2;  $r = 0.97-0.99$ ,  $s = 0.04-0.05$ ).

One should note that stability constant data for many metal chelates are scarce owing to the complexity of their experimental determination. Therefore, the solution of the reverse problem, *i.e.*, evaluation of stability constants from chromatographic data, is worthwhile.

#### Molecular connectivity indices

The concept of quantitative structure-activity interrelation, based on an incremental approach and widely used in modern chemistry, allows, in principle, chromatographic properties to be estimated on the basis of the molecular topology<sup>20</sup>. The method, which uses molecular connectivity indices as the structural index<sup>8</sup>,

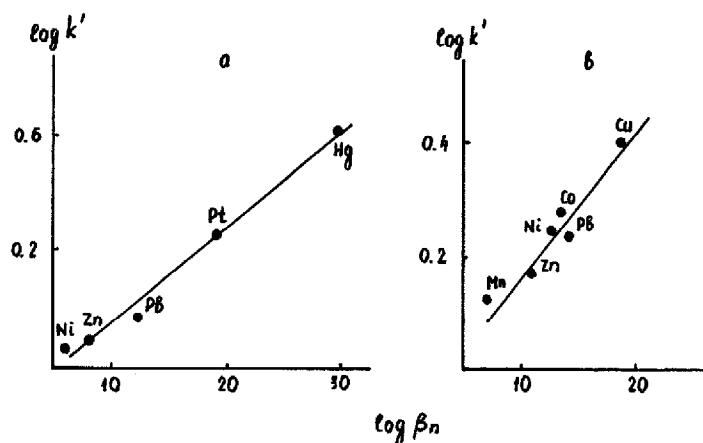


Fig. 2. Log  $k'$  values of (a) metal dibutyldithiophosphates and (b) diethyldithiocarbamates vs. stability constants. Mobile phases as in Fig. 1.

occupies an important position among the formal methods of describing molecular structure.

Tables II and III show the general type of capacity factor dependences for metal dialkyldithiophosphates with a molecular size expressed via connectivity indices of the metal and ligand (the increase in correlation factor from ethyl to octyl derivatives, in accordance with the decreasing contribution of the  $\delta$  value of the metal atom to the overall  $\chi$  value, is obvious). A similar analysis of the retention data of copper dialkyldithiocarbamates<sup>21</sup> also shows their good correlation with  $\chi$  ( $\log k' = 0.224 \chi - 3.470$ ;  $r = 0.993$ ). In general, the closest interrelation with the retention parameters of metal chelates is observed for the molecular connectivity indices. However, the superiority of  $\chi$  values over all other parameters studied is not only due to the higher correlation factors. Unlike the other parameters, the topological indices allow the contributions to the total retention and the influence of both the metal atom and ligand to be evaluated individually. According to the data in Tables II and III, the influence of the nature of the metal is most prominently expressed for hexyl and octyl derivatives and the influence of the ligand for mercury chelates.

TABLE II

DEPENDENCE BETWEEN RETENTION PARAMETERS AND MOLECULAR CONNECTIVITY INDICES FOR METAL DIALKYLDITHIOPHOSPHATES

Mobile phase: dioxane-water (90:10). DEDTP = Diethyldithiophosphate; DBDTP = di-*n*-butyldithiophosphate; DHDTP = di-*n*-hexyldithiophosphate; DODTP = di-*n*-octyldithiophosphate.

Ligand	Correlation equation	Correlation factor
DEDTP	$\log k' = 0.064 \chi - 1.680$	0.939
DBDTP	$\log k' = 0.098 \chi - 2.166$	0.941
DHDTP	$\log k' = 0.140 \chi - 3.467$	0.946
DODTP	$\log k' = 0.142 \chi - 3.702$	0.965

TABLE III

INTERRELATION BETWEEN LOG  $k'$  AND MOLECULAR CONNECTIVITY INDICES FOR METAL DIALKYLDITHIOPHOSPHATES

Mobile phase: dioxane-water (90:10).

Metal	Correlation equation	Correlation factor
Hg	$\log k' = 0.162 \chi - 4.206$	0.951
Ni	$\log k' = 0.107 \chi - 2.760$	0.933
Pb	$\log k' = 0.111 \chi - 3.980$	0.924

*Molar volume*

One of the most straightforward approaches for establishing the interrelation between retention and sorbate structure is the correlation of  $\log k'$  and molar volume<sup>22</sup>. The  $V_m$  value is directly related to the thermodynamic characteristics of the intermolecular interactions of a metal chelate in the mobile phase and to the area of molecular contact with the stationary phase. However, the limiting nature of this parameter is revealed by the fact that the estimated increase in molar volume due to branching of alkyl substituents was not confirmed experimentally by corresponding retention changes. This is related to the supposition that chelate adsorption on modified sorbents occurs at the mobile phase-modified layer interface.

Nevertheless, for metal di-*n*-alkyldithiophosphates and di-*n*-alkyldithiocarbamates, the  $\log k'$  vs.  $V_m$  dependence is met fairly well ( $r = 0.90-0.99$ ). An insufficiently good correlation for a series of metal chelates of the same ligand and different metals is obviously due to inaccuracy in the evaluation of the metal increment<sup>9</sup>.

*Carbon number*

Another topological parameter used for the quantitative evaluation of ligand structure is the number of carbon atoms in alkyl substituents ( $n_c$ ). Table IV summarizes the characteristics of  $\log k'$  vs.  $n_c$  correlation relationships. High values of

TABLE IV

CORRELATION BETWEEN CAPACITY FACTORS AND LIGAND PARAMETERS FOR METAL DIALKYLDITHIOPHOSPHATES

Mobile phase: dioxane-water (90:10).

Parameter	Parameters of correlation equation $\log k' = ax + b$								
	Hg			Ni			Pb		
	<i>a</i>	<i>b</i>	<i>r</i>	<i>a</i>	<i>b</i>	<i>r</i>	<i>a</i>	<i>b</i>	<i>r</i>
$n_c$	0.33	-1.14	0.957	0.21	-1.43	0.927	0.23	-1.53	0.929
$\sigma^*$	-3.05	-3.39	0.310	-5.57	-5.57	0.816	-5.72	-7.09	0.794
$E_s$	1.99	-1.24	0.895	2.63	-1.34	0.899	2.73	-1.42	0.905
<i>f</i>	0.16	-1.25	0.957	0.10	-1.50	0.928	0.11	-1.60	0.928
$\pi$	0.66	-1.15	0.956	0.43	-1.44	0.936	0.45	-1.54	0.931

the correlation factors indicate a good predictive ability of retention models based on the topological principle of describing the chelate molecule structure.

The physical meaning of the correlation between retention parameters and alkyl substituent chain length consists in increasing the solvophobic effect in the mobile phase and the total energy of hydrophobic interactions with the stationary phase, leading to an increase in retention. The selectivity of the separation of metal dithiophosphates increases monotonously from methyl to octyl derivatives.

#### *Induction constants*

The induction effect of substituents must directly influence the electron density of donor atoms and, hence, their capability to participate in the specific interactions in the mobile phase. A linear correlation of  $\log k'$  values with  $\sigma^*$  is observed for small-sized substituents only, however, because, as the alkyl chain length grows, (i) the induction effect rapidly attenuates and (ii) the contribution of hydrophobic adsorption becomes significant. Therefore, the application of this parameter for an *a priori* evaluation of the retention of metal chelates with alkyl substituents is limited by the comparatively small number of carbon atoms in a ligand.

#### *Steric constants*

This parameter is of interest mainly due to the influence of steric effects on the energy of specific interactions in the mobile phase. Of importance also is the decrease in contact area between a chelate molecule and the alkyl-modified layer and the probability of entry of a molecule into the sorbent surface layer when the branching of substituents increases (for steric reasons). For example, according to published data<sup>21</sup>, copper dialkyldithiocarbamates with branched substituents have slightly higher mobilities than their linear analogues.

The data in Table IV demonstrate a good interrelation between the retention parameters of metal dialkyldithiophosphates and  $E_S$  values. However, as the number of carbon atoms increases, the effect of this parameter levels off (Fig. 3). This is explained by two factors, in our opinion. First, the contribution of substituent hydrophobic interactions with the stationary phase to retention becomes prevalent and for non-linear substituents with larger  $E_S$  values  $k'$  does not increase, but remains almost unchanged (curve 1). Second, the steric effect itself ceases to change beginning from *n*-butyl derivatives, and the chelate retention continues to increase (curve 2).

#### *Hydrophobic and fragmentary hydrophobic constants*

Like the distribution constants considered above, both of these parameters describe the hydrophobic nature of a molecule. The difference lies in the fact that the Hansch ( $\pi$ ) and Rekker ( $f$ ) constants allow the hydrophobic nature of structural fragments to be estimated individually. There is no difference in the physical meaning of these parameters. The  $\pi$  and  $f$  values are obtained in the same manner, namely by correlation with the experimental values of  $\log K_D$  with the subsequent isolation of the contribution of some particular structural fragment to the integral value of the hydrophobic parameter<sup>13</sup>. By using the Rekker constants one can, however, more accurately evaluate the hydrophobicity (the Hansch method does not differentiate the contributions of methyl and methylene groups).

Hence, one can reasonably expect the correlation between  $\log k'$  and  $f$  or  $\pi$  values

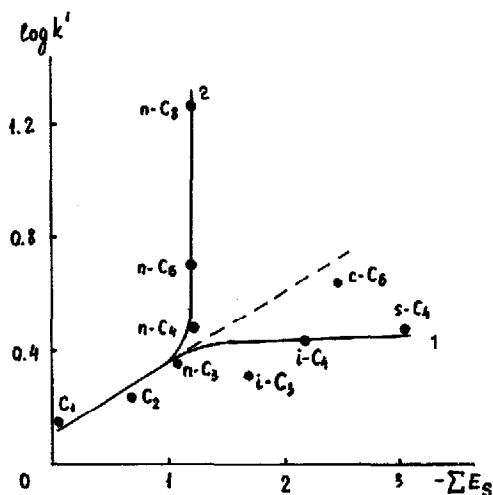


Fig. 3. Dependence of the capacity factors of mercury dialkyldithiophosphates on the steric effect of the alkyl substituents. Dioxane-water (80:20). For curves 1 and 2, see text.

to be not worse, in any case, than that between  $\log k'$  and  $\log K_D$ . This is seen from the data in Table IV. Note that there is a large body of  $f$  and  $\pi$  data for functional groups in the literature.

#### *Effective charge of metal atom*

It is generally accepted that the greater the effective charge on a metal atom, the higher is the effective charge on donor atoms and the higher is the ability of the chelate to undergo specific intermolecular interactions in the chromatographic system<sup>1</sup>. However, the values of the correlation factors obtained for dependences between  $k'$  and  $\rho_M$  have shown that the latter parameter (while possessing good heuristic functions in normal-phase chromatography<sup>2,3</sup>) has only limited application for predicting the chromatographic properties of metal chelates in reversed-phase TLC. This may be related to the fact that the relative contribution of specific interactions, especially for the chelates of the S,S-type, is less significant in this variant of liquid adsorption chromatography.

#### *Ratio of electronegativity to metal ion radius*

This parameter characterizes the degree of electron density transfer from donor atoms of the ligand to the metal atom, *i.e.*, the energy of their specific interactions in the mobile phase. However, this parameter also showed low applicability to the chelates studied ( $r < 0.6$ ), although it can be applied to metal chelates with more polar donor atoms (*e.g.*, porphyrinates<sup>24</sup>).

#### *Orbital electronegativity of metal atom*

The orbital electronegativity values (or the softness parameters) are well correlated with the extraction, distribution and stability constants of metal chelates formed by sulphur-containing reagents and soft (by Pearson<sup>26</sup>) metals. Hence, it is also logical to use  $E_n$  for calculating the retention parameters for a given type of chelate.



The respective correlation dependences for metal diethyldithiocarbamates and diethyldithiophosphates, described by the equation

$$\log k' = -aE_n + b$$

are shown in Fig. 4.

The analysis of these dependences showed that the greatest influence of the nature of the metal on the chromatographic properties of dialkyldithiophosphates (in terms of  $a$  values) is observed for hexyl and octyl derivatives. Hence, one can recommend dihexyl- and dioctyldithiophosphoric acids for practical purposes.

The high values of the correlation factors and the accessibility of  $E_n$  values make it possible to calculate the chelate retention parameters based on the preliminary experimental determination of these values for three or four complexes.

#### *Metal increment in distribution constant*

The distribution constant, having an additive character, can be presented as a sum of contributions of the groups and atoms in a molecule of a given compound. With chelates, the metal contribution (increment),  $\Delta_M$ , can be calculated to a first approximation as

$$\Delta_M = \log K_D^{ML_n} - n \log K_D^{HL}$$

where  $K_D^{ML_n}$  and  $K_D^{HL}$  are distribution constants of the metal chelate and chelating reagent, respectively. It follows from this equation that, together with the existence of a linear dependence between  $\log k'$  and  $\log K_D^{ML_n}$ , the dependence

$$\log k' = a\Delta_M + b$$

must be met. Indeed, the correlation between  $\log k'$  and  $\Delta_M$  for chelates presented in

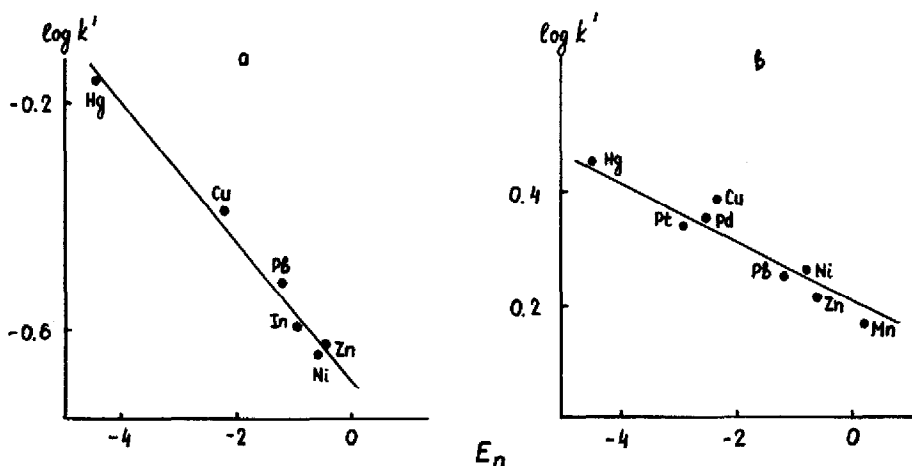


Fig. 4.  $\log k'$  vs.  $E_n$  relationships for (a) metal diethyldithiophosphates and (b) diethyldithiocarbamates. Mobile phases as in Fig. 1.

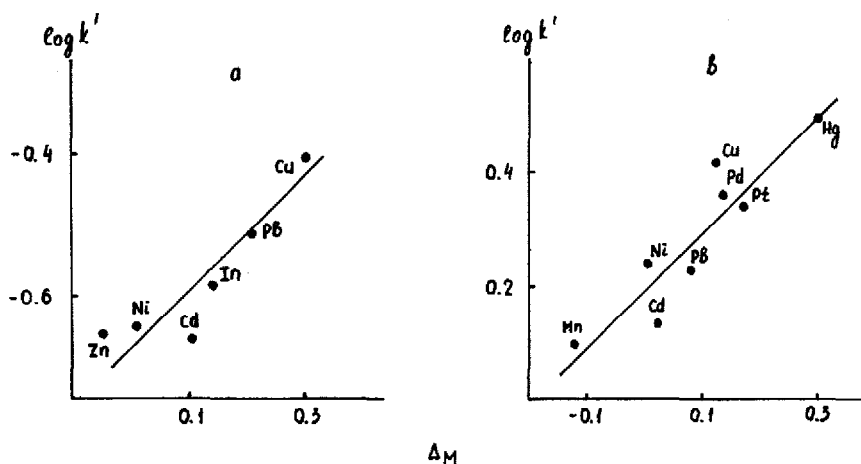


Fig. 5. Plots of  $\log k'$  and metal increment for (a) diethyldithiophosphates and (b) diethyldithiocarbamates. Mobile phases as in Fig. 1.

Fig. 5 is confirmed. It is important to note that the metal increments can be found by calculations based on known characteristics of metal chelates (effective metal charge, effective polarizability of metal and donor atoms)<sup>7</sup>.

#### Comparison of various parameters

The parameters considered can be subdivided into three groups: (i) parameters characterizing the chelate molecule as a whole ( $K_D$ ,  $\beta_m$ ,  $\chi$ ,  $V_m$ ); (ii) parameters related to the ligand structure ( $n_C$ ,  $\sigma^*$ ,  $E_s$ ,  $\pi$ ,  $f$ ); and (iii) parameters describing the metal atom properties ( $\rho_M$ ,  $\chi_M/r$ ,  $E_n$ ,  $\Delta_M$ ).

As one would expect, the chromatographic behaviour of metal chelates in reversed-phase TLC is best described by parameters in the first group. An advantage of molecular parameters is that they allow both relative and absolute retentions to be estimated and the influence of both the nature of the metal and the ligand structure to be characterized. However, the most useful parameters, in our opinion, are molecular connectivity indices, for which the highest correlation coefficients with the retention parameters were obtained. The predictive ability of  $\chi$  values was additionally confirmed with another class of chelates, metal dialkyldithiophosphinates. The comparison of experimental and calculated capacity factors showed a satisfactory reliability of such a prediction (Fig. 6;  $r = 0.91$ ,  $s = 0.04$ ).

It should be noted that  $\chi$  parameters can be obtained by computational methods irrespective of the molecule complexity. The empirical calculations of distribution and stability constants are still a non-trivial procedure.

The range of problems solved by using fragmental parameters (groups ii and iii) is narrower, however. These parameters allow the prediction of the elution sequence for a single type of chelate of the same metal or for chelates of the same class only. Nevertheless, these parameters help in solving some practically important problems such as the optimization of the chelating reagent.

The applicability of induction and steric constants for metal chelates with alkyl substituents is limited, as in normal-phase chromatography<sup>23</sup>, by compounds having

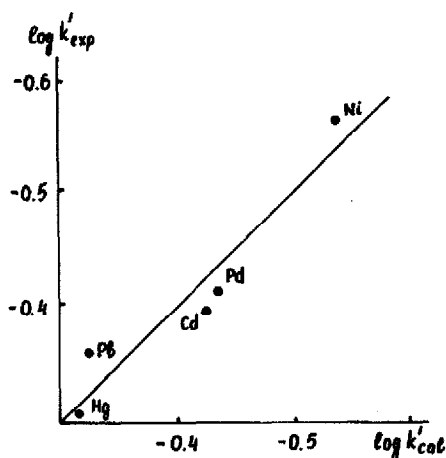


Fig. 6. Prediction of the retention of metal dipropylthiophosphinates based on the  $\log k' = a\chi + b$  model. Dioxane-water (90:10).

a small number of carbon atoms. These parameters, however, can hopefully be used not only independently, but also simultaneously, if one applies two-dimensional models of the type

$$\log k' = a + b\sigma^* + cE_s$$

Note also that  $\sigma^*$  and  $E_s$  values are sensitive to isomerism of the alkyl chain.

In contrast,  $n_c$ ,  $f$  and  $\pi$  are not sensitive to branching of the molecular structure, but describe well the chromatographic properties of chelates with linear substituents with any number of carbon atoms. Hence, the ligand parameters supplement each other well. The correlation between retention and ligand structure parameters allows the conclusion that the retention of metal chelates is determined to a great extent by the size and hydrophobic nature of a molecule, which is in good agreement with the solvophobic theory<sup>25</sup>.

The correlation dependences for metal parameters have the lowest correlation factors. This is due to the fact that, together with the specific interactions with polar components of the mobile phase, the retention of the metal chelates studied is also influenced by hydrophobic interactions. The latter are not related directly with the electron-acceptor properties of metal atoms.

A more detailed analysis of structural parameters and separation of the most meaningful ones should allow the retention mechanism for metal chelates in reversed-phase TLC to be studied more thoroughly.

## CONCLUSION

We have shown the possibility of using one-dimensional relationships for the *a priori* estimation of chelate retention. However, despite the good predictive ability in most instances, dependences of such a type cannot be considered to be universal. This is due to the limited nature of the approach itself, which takes advantage of only one of

the possible parameters. No one parameter considered takes into account completely enough all chelate structure effects. A complete quantitative model of the reversed-phase TLC of metal chelates must be based on a multi-dimensional approach to the dependence of chromatographic properties on structure and on chromatographic experimental conditions. The development of such a model is our next task.

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