A CONTRIBUTION TO THE DESCRIPTION
OF THE RETENTION MECHANISM OF METAL CHELATES
DURING THEIR REVERSED-PHASE CHROMATOGRAPHY

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Mercury(II) diethyldithiocarbamate was chromatographed on silica gel with chemically bonded octadecyl groups using aqueous mixtures with methanol, acetonitrile, dioxane, and tetrahydrofuran, respectively, as the mobile phase, and the dependence of logarithm of the capacity ratio (k) on the volume fraction of water in the binary mobile phase was examined. Also, the dependence of k on the liquid–liquid extraction distribution ratio in an aqueous methanol–n-alkane extraction system was investigated for Cu, Co, Ni, Pb, and Hg diethyldithiocarbamates. Both kinds of dependence are linear, which suggests that the retention of the electroneutral metal chelates during the reversed-phase liquid chromatography on a nonpolar chemically bonded phase is due to the solvophobic effect.

The mechanism of the solute retention during reversed-phase liquid chromatography (RP-LC) depends on the type of the stationary phase used, composition of the mobile phase, and nature of the solute. The mechanisms so far suggested have been verified always for one or a few groups of substances, usually simple organic compounds. The mechanism of retention in RP-LC has been studied extensively for a variety of solutes by Horváth and coworkers[1-4], Guiochon and coworkers[5,6], and other authors[7-10], who either described the degree of solute retention, expressed by the capacity ratio k, in thermodynamic terms[1,2,4,5], or examined the relations between the capacity ratio of solute and other quantities such as the mobile phase composition or the distribution constant for a liquid–liquid extraction system[5-7].

The mechanism of retention of metal chelates was of interest to us in connection with our seeking for the optimum composition of the mobile phase for their RP-LC treatment[11]. Since for this optimization the knowledge of the thermodynamic values is not important, we resorted to the latter of the two approaches for establishing the mechanism of the metal chelate retention by the sorbent with bonded nonpolar groups.

In the present work, we have therefore studied the chromatographic behaviour of ML_2 diethyldithiocarbamates with M = Cu(II), Co(II), Ni(II), Pb(II), and Hg(II),

and $L = (C_2H_5)_2$—N—CS—S$^-$, on silica gel modified with octadecyl groups as the stationary phase, with a view to establishing the relation between the capacity ratio and the composition of the mobile phase; we examined also the relation between the capacity ratios and the distribution ratios of the metals for the extraction of their diethyldithiocarbamates from an aqueous phase into a saturated hydrocarbon organic phase.

EXPERIMENTAL

Chemicals and Apparatus

The solvents were purified conventionally[11]. Solutions of Cu, Co, Ni, Pb, and Hg diethyldithiocarbamates were prepared from aqueous solutions of nitrates or perchlorates of the metals by extraction after adding sodium diethyldithiocarbamate *p.a.* (Lachema, Brno) at pH 7·6 (citrate buffer)[12]. Chloroform was freed from phosgene according to ref.[13]. A sample of a C_{10}—C_{13} n-alkane mixture, obtained from the Department of Petroleum Technology and Petrochemistry of our Institute, and n-hexane (Reakhim, USSR) were purified by filtration over an activated silica gel column, whereby impurities absorbing in the UV region were removed.

A Varian Model 4 000 liquid chromatograph (Varian, Palo Alto, USA) equipped with a column packed with Separon SI C 18 (Laboratorní přístroje, Prague) was used; column 250 mm, 4 mm i.d., sorbent particle size $d_p = 10$ μm; a UV 254/280 nm detector (Varian), cell volume 8 μl. Metal diethyldithiocarbamate solutions for chromatography were prepared from known amounts of the metal nitrates by quantitative extraction at pH 6 into pure chloroform. The solution obtained was evaporated just to dryness in a vacuum rotary evaporator at room temperature, and the residue was dissolved in a small known volume of pure tetrahydrofuran or dioxane. Ten μl of this solution were injected through a silicone rubber septum. The dead time t_M was determined from the time it took an air bubble added to the mobile phase to pass the column; the use of thiourea, recommended[14] for the determination of the dead volume in RP-LC in conjunction with a photometric detector, was unsuitable because the retention volumes were too large and the resulting peaks exhibited pronounced tailing.

The absorbances, requisite for the determination of the chelates, were measured on a VSU 2 spectrophotometer (Carl Zeiss, Jena) in quartz cells.

Procedure for Determination of Distribution of Diethyldithiocarbamates Between Aqueous and Organic Phases

To 10 ml of hydrocarbon phase was added 100 μl of chloroform solution of metal diethyldithiocarbamate and the whole was shaken with 10 ml of aqueous phase for 10 min. The hydrocarbon phase contained a mixture of n-alkanes ($\varphi = 0\cdot5$) and n-hexane ($\varphi = 0\cdot5$), the aqueous phase was a mixture of methanol ($\varphi = 0\cdot82$) with water. The absorbance of the organic phase was measured at the wavelength of the metal chelate absorption maximum in n-alkane, *viz.* 265 (Co), 320 (Ni), 267 (Pb), 269 (Cu), and 270 nm (Hg). The chelate concentration in the organic phase was calculated from the prior derived straight line equation for the calibration dependence of absorbance on chelate concentration. The region of validity of this linear relationship was found for the various chelates to be $0\cdot1$—$1\cdot2$ mg l^{-1} (Cu, Co), $0\cdot15$—$1\cdot5$ mg l^{-1} (Ni), and 0·5 to 5 mg l^{-1} (Pb, Hg).

RESULTS AND DISCUSSION

Assuming that the retention of ML_2 metal chelates on the reversed phase constituted by silica gel with chemically bonded octadecyl groups involves two mechanisms, viz. the solvophobic and the silanophobic mechanisms (e.g., ref.[2]), the resultant capacity ratio of the metal chelate can be written as

$$k = k_1 + k_2 , \qquad (1)$$

where k_1 and k_2 are the contributions to the retention from the two mechanisms, respectively. It has been shown[15] that for retention caused by the solvophobic effect, $\log k$ is a linear function of the volume fraction of the water in the binary mobile phase (φ_{H_2O}), so that

$$k_1 = a \exp \left(b \varphi_{H_2O} \right) . \qquad (2)$$

For sorption on unmodified silica gel, where the silanophilic interaction plays the major role, the relation

$$k_2 = \left(c + d \varphi_X \right)^{-1} \qquad (3)$$

holds true[16] (φ_X is the volume fraction of the more polar component in the binary mobile phase system). Substituting in Eq. (1) we thus obtain

$$k = a \exp \left(b \varphi_{H_2O} \right) + \left(c + d \varphi_{H_2O} \right)^{-1} ; \qquad (4)$$

evidently, the dependence of $\log k$ on φ_{H_2O} will not be linear if both retention mechanisms play a marked role.

According to Jandera and coworkers[5], the dependence of $\log k$ on the volume fraction of the organic component in a binary mixture with water can be written as

$$\log k = a - n \log \varphi_{org} + d \varphi_{org}^2 \qquad (5)$$

which often reduces to Eq. (2), because the quadratic term can be omitted.

We measured, for mercury(II) diethyldithiocarbamate, the dependence of $\log k$ on the volume fraction of water in its mixtures with methanol, acetonitrile, dioxane, and tetrahydrofuran, respectively (Fig. 1). Linear relations were obtained with high correlation coefficients (0·996, 0·999, 0·998, and 0·969 for the four systems, respectively). The lower value of the correlation coefficient for the water–tetrahydrofuran mixture can be understood in view of the observation of Martire and Boehm[10], who found a relation between the capacity ratio of solute and the mobile phase composition, analogous to Eq. (2) which was rigorously valid only for mixtures of highly polar solvents; and the polarity of the solvents used by us decreases in order

methanol (solvent strength ε^0 0·95), acetonitrile (0·65), dioxane (0·56), tetrahydrofuran (0·45) (ref.[17]).

The linear dependence of log k on the volume fraction of water in the mobile phase system thus suggests that the retention of the metal diethyldithiocarbamates (and, perhaps, all electroneutral metal chelates) is largely due to the solvophobic effect.

If this is true, then the interactions occurring during the retention of chelates on the reversed phase used should be similar to those occurring during the extraction of the chelates from an aqueous to an octadecane organic phase, and the capacity ratio of the chelates in RP-LC should be a simple function of the distribution constant K_D or distribution ratio D_c established for this extraction.

From the relation for the retention volume V_R in LSC,

$$V_R = V_M(k + 1) = V_m + D_g m_s, \tag{6}$$

where V_M is the dead volume, V_m is the mobile phase volume in the column, m_s is the weight of the stationary phase, and D_g is the distribution coefficient of the chelate $(D_g = \eta_{ML_2,s}/[ML_2]_m$, where $\eta_{ML_2,s}$ is the amount of substance content of the chelate in the stationary phase, in mmol g^{-1} for instance, and $[ML_2]_m$ is the concentration of the chelate in the mobile phase, e.g., in mol l^{-1}), k can be expressed as

$$k = (V_m/V_M - 1) + D_g r, \tag{7}$$

where $r = m_s/V_M$. If the chelate extraction from the aqueous phase into octadecane and the chelate sorption from the same aqueous phase onto a sorbent with chemically bonded octadecyl groups involve the same type of interaction, then the metal distribu-
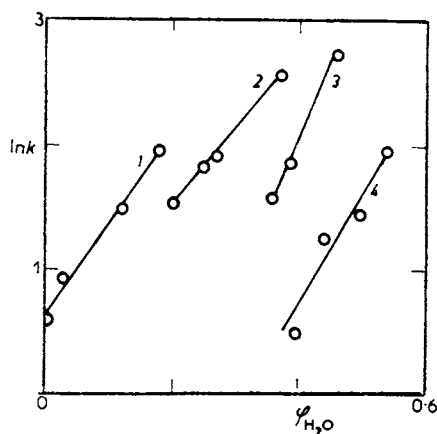

FIG. 1

Dependence of logarithm of capacity ratio (ln k) of mercury (II) diethyldithiocarbamate on the volume fraction of water in mixture with methanol 1, acetonitrile 2, dioxane 3, and tetrahydrofuran 4

tion ratio D_c for the liquid–liquid equilibrium $(D_c = c_{M,org}/c_{M,aq})$ and the metal distribution coefficient for the liquid–solid equilibrium should be interrelated simply as $D_g = jD_c$, and so

$$k = (V_m/V_M - 1) + r'D_c, \tag{8}$$

where $r' = jr$.

The dependence of k on D_c thus should be linear, and for $V_m = V_M$ the plot should pass through the origin. Actually, however, a small negative intercept can be expected $(V_m/V_M < 1)$.

The assumption of similar interactions in the two types of distribution is borne out, e.g., by the results of Lochmüller and Wilder[18] and, for nonpolar substances

TABLE I

Reversed-phase liquid chromatography and liquid–liquid extraction characteristics of metal diethyldithiocarbamates

Metal	k	$A_s{}^a$	D_c	$\log K_{ex}{}^b$
Co	3·2	3·71	0·360	2·33
Ni	3·5	3·04	0·644	11·58
Pb	5·3	5·80	1·021	7·77
Cu	5·2	3·60	1·870	13·70
Hg	7·1	2·50	3·198	32·12

^{a} Peak asymmetry factor; ^{b} K_{ex} is the chelate extraction constant in the CCl_4–H_2O system.
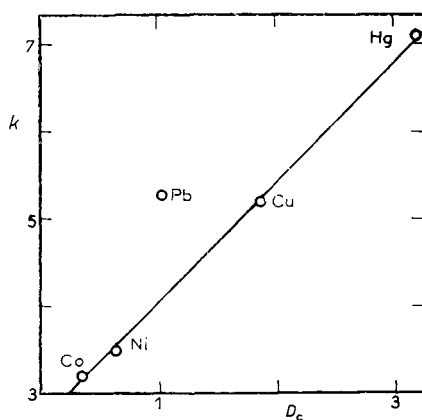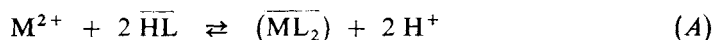

FIG. 2

Dependence of capacity ratio (k) of metal diethyldithiocarbamates in RP system on their distribution ratio (D_c) for the extraction from aqueous methanol into n-alkane

and (water + methanol)–n-alkane and (water + methanol)–RP C 18 systems, by the study of Hammers and coworkers[7]. In the two cases, the dependence of the capacity ratio k on the distribution constant K_D was examined for simple organic substances (non-protolytes) for which $K_D = D_c$.

The D_c values for Cu(II), Co(II), Ni(II), Pb(II), and Hg(II) diethyldithiocarbamates were measured by us in an n-alkane–(water + methanol) system with $\varphi_{methanol} = 0.82$. The aqueous phase thus was the same as used for the chromatographic study; the n-alkane system was a mixture of $C_{10}H_{22}$ through $C_{13}H_{28}$ hydrocarbons diluted with the same volume of n-hexane; thus the two phases after the extraction could be quantitatively separated.

The D_c values obtained are given in Table I, the dependence of k on D_c for the diethyldithiocarbamates is shown in Fig. 2.

The lead chelate resides on the column longer than as corresponds to the observed linear dependence of k on D_c. This can be explained by the occurrence of some additional interaction during the chromatographic process, as also borne out by the peak asymmetry factor being higher for the Pb chelate than for the remaining chelates (Table I). A similar anomaly in a series of values characterizing the distribution of metal diethyldithiocarbamates between two phases can also be observed for the extraction constants K_{ex}, i.e., the equilibrium constants of the two-phase (water––tetrachloromethane) equilibrium[19]

$$M^{2+} + 2\,\overline{HL} \rightleftharpoons (\overline{ML_2}) + 2\,H^+ \qquad (A)$$

(bars label species in the organic phase). Generally, the course of the K_{ex} values is the same as the chromatographic elution order of the chelates.

The straight line intercept in Fig. 2 is 2·65, which is clearly due to some error in the experimental V_M value $(V_M < V_m!)$. For the chromatography of simple nonpolar organic substances, Hammers and coworkers[7] obtained a straight line which passed through the origin; in fact, however, the capacity ratio was calculated by them via the experimental V_m value rather than the V_M value.

It can be thus concluded, based on the observed dependences of the capacity ratio on the mobile phase composition and on the distribution ratio, that the retention of metal diethyldithiocarbamates during their reversed-phase liquid chromatographic treatment is caused by the solvophobic interaction; it is reasonable to assume that this applies to all electroneutral metal chelates.

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