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SELECTIVITY OF COMPLEXING GAS CHROMATOGRAPHIC STATIONARY PHASES CONTAINING LANTHANIDE β-DIKETONATES

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SUMMARY

The Rohrschneider–McReynolds series of organic compounds has been used to determine the polarity of gas chromatographic stationary phases containing tris-β-diketonates of praseodymium and europium, dissolved in poly(dimethylsiloxane). The selectivity of the stationary phases studied has been characterized by using the differential excess partial molar free energy of mixing within the temperature range of 90–130°C. Changes in selectivity observed with increasing temperature are discussed in the context of the proposed complexation scheme.

INTRODUCTION

The application of stationary phases containing metal coordination compounds to the gas chromatographic (GC) separation of organic substances has been the subject of many publications and reviews[1-5]. In certain papers[6,7] the authors pointed out the high selectivity of separation for selected series of compounds used as samples.

The purpose of the present work was the qualitative and quantitative evaluation of the "polarity" and "selectivity" of stationary phases containing β-diketonates of praseodymium and europium, by employing the Rohrschneider–McReynolds classification of stationary phases[8-10], as modified by Golovnya and Micharina[11,12].

EXPERIMENTAL

Materials

The columns were 250 cm × 3 mm I.D. Pyrex glass tubes, filled with the following packings: 10% SE-30 (the reference column); 10% SE-30 plus 0.1 mmol/g Pr(fod)$_3$; 10% SE-30 plus 0.1 mmol/g Eu(fod)$_3$ on Gas-Chrom Q, 100–120 mesh.

The Rohrschneider–McReynolds series of standard compounds and the homologous series of *n*-alkanes were commercial analytical-grade reagents. The lanthanide chelates, Pr(fod)$_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)-praseodymium] and Eu(fod)$_3$ [tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)europium], were obtained from Merck (Darmstadt, F.R.G.).

Apparatus

A CHROM-5 research chromatograph from Laboratorní Přístroje (Czechoslovakia) with a flame ionization detector was used. In order to measure the column temperature accurately, a calibrated mercury thermometer was inserted into the column oven. The flow-rates of the carrier gas (helium), hydrogen and air were 35, 30 and 400 cm³/min, respectively, as measured at ambient temperature and pressure with a bubble flowmeter. The oven was operated isothermally at 90, 100, 110, 120 and 130°C.

Procedure

About 0.1–0.3-μl charges of 5% pentane solutions of standard compounds were injected into the gas chromatograph. The sample size was adjusted to keep all peaks on scale at the maximum sensitivity of the detector unit.

The dead-time, t_m, and the slope of the *n*-alkane plot, b (see eqn. 2), were determined with a linear regression procedure[13]. Values of the Kováts retention indices, I_i, were determined for the series of samples studied on individual stationary phases.

RESULTS AND DISCUSSION

In Table I values of the retention indices, I_i, are listed, determined at 120°C on the stationary phases for a series of the Rohrschneider–McReynolds standard compounds. *n*-Butanol, 2-pentanone, pyridine, 2-methyl-2-pentanol and 1,4-dioxane show considerably higher index values when chromatographed on the stationary phases containing lanthanide chelates than on the reference SE-30 stationary phase. The remaining standard substances, *i.e.*, benzene, 1-nitropropane, 1-iodobutane, 2-octyne and *cis*-hydrindane showed no apparent difference in their retention index values when the results obtained on the complexing and the reference stationary

TABLE I

RETENTION INDEX VALUES, I_i, FOR THE ROHRSCHNEIDER–McREYNOLDS SERIES OF SOLUTES, MEASURED ON THE COMPLEXING AND REFERENCE STATIONARY PHASES AT 120°C

No.	Standard substance	Stationary phase		
		10% SE-30	*10% SE-30 + 0.1 mmol/g Eu(fod)₃*	*10% SE-30 + 0.1 mmol/g Pr(fod)₃*
1	Benzene	680	673	683
2	*n*-Butanol	657	1052	920
3	2-Pentanone	662	1039	925
4	1-Nitropropane	708	732	735
5	Pyridine	738	1225	1088
6	2-Methyl-2-pentanol	712	1012	887
7	1-Iodobutane	812	818	853
8	2-Octyne	880	886	872
9	1,4-Dioxane	690	850	821
10	*cis*-Hydrindane	1002	1010	1010

phase were compared. In accordance with the Rohrschneider–McReynolds classification of stationary phases in GC, one can conclude that the lanthanide chelate-containing stationary phases are "polar" with respect to nucleophilic compounds, *i.e.*, toward nitrogen bases, alcohols, ketones and ethers. The same stationary phases appear to be "non-polar" with respect to classes represented by benzene, 1-nitropropane, 1-iodobutane and 2-octyne, able to form π-complexes or to participate in dipole–dipole interactions. Thus the above-mentioned classes of organic compounds do not specifically interact with the lanthanide chelates dissolved in poly(dimethylsiloxane), under the applied chromatographic conditions.

In the Rohrschneider–McReynolds system of stationary phase classification, selectivity is based on the differences in retention indices, measured for each standard compound, on two columns; the first column contains the stationary phase investigated, and the second one is packed with the reference phase, *i.e.*, squalane.

In this work, a poly(dimethylsiloxane) SE-30 stationary phase was used as the reference. The values of ΔI_i, representing the difference in the retention indices of a standard test compound, i, obtained on the investigated stationary phases and on SE-30, are given in Table II:

$$\Delta I_i = I_i^{\text{Ln-chelate}} - I_i^{\text{SE-30}} \tag{1}$$

High values of ΔI_i were obtained on the complexing stationary phases, and increased in the following sequence of standard substances:

pyridine $>$ n-butanol $>$ 2-pentanone $\geqslant$ 2-methyl-2-pentanol $\geqslant$ 1,4-dioxane

High ΔI_i values reflect the efficiency of the intermolecular interactions between the stationary phase and solutes. One can conclude that the stationary phases investigated are considerably selective towards nucleophilic compounds, which contain the following functional groups:
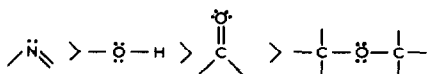

TABLE II

RETENTION INDEX DIFFERENCES, $(\Delta I_i)_{a,r}$, DETERMINED FOR THE STATIONARY PHASES CONTAINING EUROPIUM AND PRASEODYMIUM CHELATES

No.	Standard substance	ΔI	
		$Eu(fod)_3$	$Pr(fod)_3$
1	Benzene	−7	2
2	n-Butanol	395	263
3	2-Pentanone	377	263
4	1-Nitropropane	24	27
5	Pyridine	487	350
6	2-Methyl-2-pentanol	300	175
7	1-Iodobutane	6	41
8	2-Octyne	6	12
9	1,4-Dioxane	160	131
10	cis-Hydrindane	8	8

TABLE III

VALUES OF b AND $\Delta G_{(CH_2)}$, DETERMINED IN THE TEMPERATURE RANGE OF 90–130°C

Stationary phase	Temperature (°C)	b	$-\Delta G_{(CH_2)}$ (kcal/mol)
SE-30	90	0.324	0.538
	100	0.292	0.498
	110	0.274	0.480
	120	0.250	0.450
	130	0.222	0.409
SE-30 + 0.1 mmol/g Eu(fod)$_3$	90	0.288	0.478
	100	0.278	0.459
	110	0.262	0.447
	120	0.235	0.440
	130	0.227	0.419
SE-30 + 0.1 mmol/g Pr(fod)$_3$	90	0.302	0.501
	100	0.283	0.484
	110	0.266	0.467
	120	0.248	0.446
	130	0.236	0.435

The other standard solutes do not show any substantial difference when chromatographed on the complexing or the non-complexing stationary phase. It was established that the lanthanide chelates neither interact with aromatic and unsaturated systems, nor with molecules capable of dipole–dipole interactions.

In Table III are presented values of b and $\Delta G_{(CH_2)}$, which characterize the chromatographic retention of n-alkanes on the stationary phases studied

$$b = \log \frac{V_g (n + 1)}{V_g (n)} \tag{2}$$

$$\Delta G_{(CH_2)} = -2.3RTb \tag{3}$$

where $V_g (n + 1)$ and $V_g (n)$ are the specific retention volumes of n-alkanes with n and $n + 1$ carbon atoms in the molecule, respectively, $\Delta G_{(CH_2)}$ is the partial molar free energy of solution of a $-CH_2-$ group, R is the gas constant and T is the column temperature in K.

From the results noted in Table III it can be concluded that the presence of 0.1 M concentrations of lanthanide chelates does not considerably influence the dispersive properties of the stationary phases. The heptafluoropropyl radicals ($-C_3F_7$) present in the lanthanide chelate structure seem to cause a slight decrease in the b and $\Delta G_{(CH_2)}$ values.

A more detailed insight into the selectivity of the stationary phases studied can be gained from a thermodynamic approach[14], which defines selectively as the difference in the excess partial molar free energy of mixing for solute i

$$\delta(\Delta G_i^e)_{s,r} = (\Delta G_i^e)_s - (\Delta G_i^e)_r \tag{4}$$

where (ΔG_i^e) is the excess partial molar free energy of mixing for solute i, and s and r refer to the stationary phase studied and reference, respectively.

Under isothermal conditions, the selectivity of the two stationary phases with respect to solute i is determined as the difference in the partial molar free energies of solution, ΔG_i[11]

$$\delta(\Delta G_i^e)_{s,r} = (\Delta G_i)_s - (\Delta G_i)_r \qquad (5)$$

assuming that

$$(\Delta G_i)_s = (\Delta G_i^e)_s - (\Delta G_i)_{vap} \qquad (6)$$

and

$$(\Delta G_i)_r = (\Delta G_i^e)_r - (\Delta G_i)_{vap} \qquad (7)$$

where $(\Delta G_i)_{vap}$ is the free molar energy of vaporization of solute i. It becomes evident that one can use the ΔG_i parameters instead of those of ΔG_i^e, if one substracts eqn. 7 from eqn. 6. The numerical values of $\delta(\Delta G_i^e)_{s,r}$ were calculated with the help of eqn. 8

$$\delta(G_i^e)_{s,r} = -2.3\ RT\left[\frac{I_s - 100\ n_s}{100} \cdot b_s - \frac{I_r - 100\ n_r}{100} \cdot b_r + \right.$$

$$\left. + \log \frac{V_g n\ (s)}{V_g n\ (r)} + \log \frac{\delta_s}{\delta_r} \right] \qquad (8)$$

where n_s and n_r denote the number of carbon atoms in the n-alkanes used for calculation of the retention indices for a solute i, the subscripts s and r refer to the studied and reference stationary phases, respectively; $V_g n$ is the specific retention volume of a n-alkane having n carbon atoms in the molecule and δ is the density of the stationary phase.

Since $\delta_s/\delta_r \approx 1$, the last term in eqn. 8 was neglected in this work.

From Fig. 1a and b, the highest values of $\delta(\Delta G_i^e)$ were observed for pyridine, then in descending order, for n-butanol, 2-pentanone, 2-methyl-2-pentanol and 1,4-dioxane. A slight decrease in the selectivity with increasing column temperature was observed. This behaviour can be explained by a decrease in the equilibrium constant for formation of the lanthanide chelate–nucleophile adduct. The low selectivity values for benzene, 1-iodobutane, 2-octyne, 1-nitropropane and cis-hydrindane suggest that the specific interactions between these solutes and the stationary phases investigated are either non-existent or very weak.

Comparing the $\delta(\Delta G_i^e)$ values obtained on the Eu(fod)$_3$- and the Pr(fod)$_3$-containing stationary phases, it can be stated that the europium-containing phase is more selective for ethers, substituted alcohols, ketones and n-alcohols than its praseodymium-containing counterpart. This behaviour can be related to differences in the ionic radii of lanthanides, as discussed by Feibush et al.[2] and by Choppin[15].
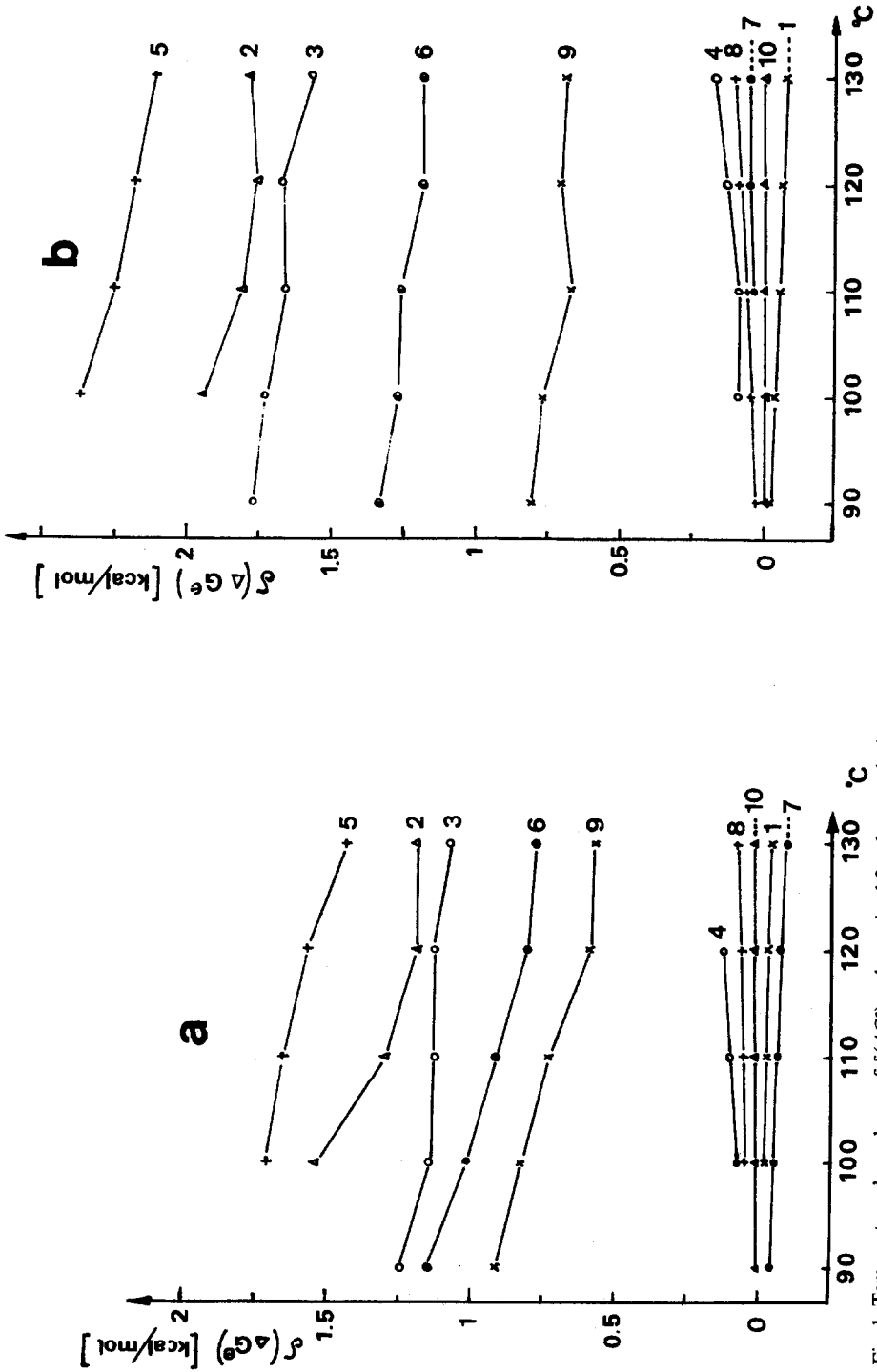
Fig. 1. Temperature dependence of $\delta(\Delta G_i^e)_{s,t}$, determined for the complexing stationary phases containing Pr(fod)$_3$ (a) and Eu(fod)$_3$ (b). Numbering of solutes as in Table I.

The data presented demonstrate that the lanthanide-containing stationary phases should find wider application in the GC of nucleophilic solutes.

CONCLUSIONS

It was demonstrated that GC stationary phases containing the lanthanide chelates, dissolved in poly(dimethylsiloxane), possess an ability to form adducts with a selected series of nucleophilic compounds.

The thermodynamic selectivities were determined for the ten standard solutes in the temperature range of 90–130°C on the stationary phases containing europium and praseodymium chelates. Considerable selectivity values were established for the following classes of solutes

nitrogen bases > *n*-alcohols > ketones > *tert.*-alcohols > ethers

although an increase in column temperature lessened this effect.

Comparison of the data obtained on the praseodymium- and europium-containing phases showed that selectivity for the test compounds used was also dependent on the lanthanide ionic radius.

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