

METAL COMPLEXES OF β -DIKETONES AS LIQUID PHASES IN GAS-LIQUID CHROMATOGRAPHY

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It was thought that the complexes between a cation and an organic ligand might have interesting properties when used as liquid phase in gas-liquid chromatography. Selective separations might be achieved and quantitative data on the interaction between the vapours and the complexes obtained. BRADFORD *et al.*¹ reported the use of a silver nitrate solution in diethylene glycol for the determination of unsaturated hydrocarbons and BARBER *et al.*² when using metallic stearates as a liquid phase observed that amines of various types have a high retention volume. CARTONI *et al.*³ investigated nickel, palladium and platinum complexes with methyl-*n*-octyl-glyoxime and dodecyl salicylalimine and showed that the retention volume of several compounds (namely amines, ketones and alcohols) which can act as a ligand towards the bound cation in these complexes is strongly increased in comparison with their behaviour on an inert column.

We are now reporting on an investigation on the behaviour, as liquid phase in gas-liquid chromatography, of complexes of symmetrical β -diketones with various metals on account of the specific reactivity of these ligands and of the property exhibited by some complexes of these ligands to bind reversibly some molecules.

β -Diketones with a low number of carbon atoms are quite volatile, but if the length of the aliphatic chain is increased, the resulting compound has a higher boiling point and its copper salt a lower melting point. Satisfactory results, as far as the chromatographic properties are concerned (*e.g.* melting point, volatility), have been obtained with the complexes of beryllium, aluminium, nickel, zinc and copper with *n*-nonyl- β -diketones.

EXPERIMENTAL

n-Nonyl- β -diketone (NdC) was prepared according to ZELLARS AND LEVINE⁴ by treating an ether solution of methyl *n*-nonyl-ketone with the ethyl ester of capric acid in the presence of sodium amide. The NdC was dissolved in methanol and poured into a warm saturated solution of copper acetate. After cooling, the copper complex with NdC was filtered off and after drying recrystallized from petrol ether. The free NdC was obtained after acidification with 3 *N* sulphuric acid.

Beryllium, aluminium, nickel and zinc complexes with NdC were made by dissolving NdC in a small amount of ethanol and in the presence of a few drops of concentrated ammonia. A concentrated solution of the metal carbonate, in the stoichiometric ratio, is added and a few drops of ammonia to keep the solution slightly

alkaline. In each case, an oil was obtained which becomes a solid mass on cooling. The complexes are soluble in ether and chloroform. They were recrystallized from ethanol and have the following melting points: $\text{Be}(\text{NdC})_2$, 53–53.5°; $\text{Al}(\text{NdC})_3$, 40–40.5°; $\text{Ni}(\text{NdC})_2$, 48–49°. The $\text{Zn}(\text{NdC})_2$ is liquid at room temperature.

All complexes have a good thermal stability and were employed in columns kept at a working temperature of 120° without appreciable bleeding. Packed columns were prepared by mixing celite with an ether solution of various complexes; their concentration was about 20%. The chromatograms were carried out with a home-made gas chromatograph, which was thermostated with an accuracy of $\pm 0.2^\circ$ and equipped with a hydrogen flame detector and nitrogen was used as carrier gas.

Homologous series of various compounds (alkanes, aromatic hydrocarbons, ketones, alcohols) were chromatographed on columns containing the complexes described above and on a column containing squalane; the latter was taken as a typical non-polar liquid phase to act as a reference for the former. Its chromatographic behaviour may be considered as ideal. All measurements were carried out at 120°.

The retention volumes of the various compounds were referred to normal heptane which was taken as a reference. Its specific retention volume, V_g at 120°, for the various phases is shown in Table I.

TABLE I

SPECIFIC RETENTION VOLUMES OF *n*-HEPTANE AT 120°, FOR VARIOUS LIQUID PHASES

Liquid phase	V_g (ml \times g ⁻¹)
Squalane	34.0
$\text{Cu}(\text{NdC})_2$	22.7
$\text{Ni}(\text{NdC})_2$	18.5
$\text{Al}(\text{NdC})_3$	24.0
$\text{Be}(\text{NdC})_2$	26.6
$\text{Zn}(\text{NdC})_2$	19.2

RESULTS

The relative retention volumes of various compounds are reported in Table II. By plotting the logarithm of relative retention volumes against the number of carbon atoms a set of straight lines are obtained.

The plot of the relative retention volumes of various compounds on metal complex columns *versus* the relative retention volume on a squalane column yields straight lines passing through the origin. In Fig. 1 the behaviour of various homologous series on $\text{Zn}(\text{NdC})_2$ and $\text{Ni}(\text{NdC})_2$ columns *versus* a squalane column is shown. Similar behaviour is observed for other metal complexes, the slope, however, being slightly different for each homologous series.

The slopes of these lines are a measure of the retardation, relative to *n*-heptane, and from these values an indication of the interaction which takes place between a set of homologous compounds and the liquid phase may be obtained. These figures are reported in Table III.

TABLE II

RELATIVE RETENTION VOLUMES *versus* *n*-HEPTANE AT 120°

Liquid phase	$Cu(NdC)_2$	$Ni(NdC)_2$	$Al(NdC)_3$	$Be(NdC)_2$	$Zn(NdC)_2$	Squalane
<i>Alkanes</i>						
C ₆	0.50	0.49	0.50	0.52	0.53	0.49
C ₇	1.00	1.00	1.00	1.00	1.00	1.00
C ₈	1.96	1.94	1.96	1.99	1.96	1.99
<i>Aromatic hydrocarbons</i>						
C ₆	1.11	0.98	1.12	1.19	1.12	0.73
C ₇	2.28	1.96	2.26	2.41	2.30	1.54
<i>Aliphatic ketones</i>						
C ₃	0.23	0.33	0.40	0.32	0.25	0.15
C ₄	0.49	0.53	0.60	0.59	0.51	0.32
C ₅	0.90	0.87	0.91	1.06	0.97	0.61
C ₆	—	1.68	1.86	2.10	1.90	1.24
<i>Tertiary alcohols</i>						
C ₄	0.33	0.35	0.26	0.37	0.53	0.22
C ₅	0.73	0.71	0.70	0.84	1.05	0.52
<i>Secondary alcohols</i>						
C ₃	0.31	0.60	0.36	0.37	0.53	0.16
C ₄	0.66	0.91	0.66	0.74	1.02	0.37
C ₅	1.31	1.75	1.15	1.35	2.05	0.72
<i>Primary alcohols</i>						
C ₁	0.24	2.04	0.65	0.46	0.30	—
C ₂	0.31	1.53	0.43	0.39	0.42	0.11
C ₃	0.61	1.96	0.58	0.68	0.81	0.24
C ₄	1.28	3.68	1.15	1.43	1.72	0.51
C ₅	2.15	6.25	1.83	—	—	0.89

TABLE III

RETARDATION FACTORS FOR $Me(NdC)_n$ COMPLEXES *versus* SQUALANE

Homologous series	$Cu(NdC)_2$	$Ni(NdC)_2$	$Al(NdC)_3$	$Be(NdC)_2$	$Zn(NdC)_2$
Alkanes	1.00	1.00	1.00	1.00	1.00
Aromatic hydrocarbons	1.70	1.32	1.52	1.53	1.50
Ketones	1.70	1.38	1.52	1.70	1.56
Tertiary alcohols	1.70	1.38	1.31	1.58	2.20
Secondary alcohols	1.78	2.40	1.67	1.34	2.84
Primary alcohols	2.43	7.10	2.10	2.64	2.43

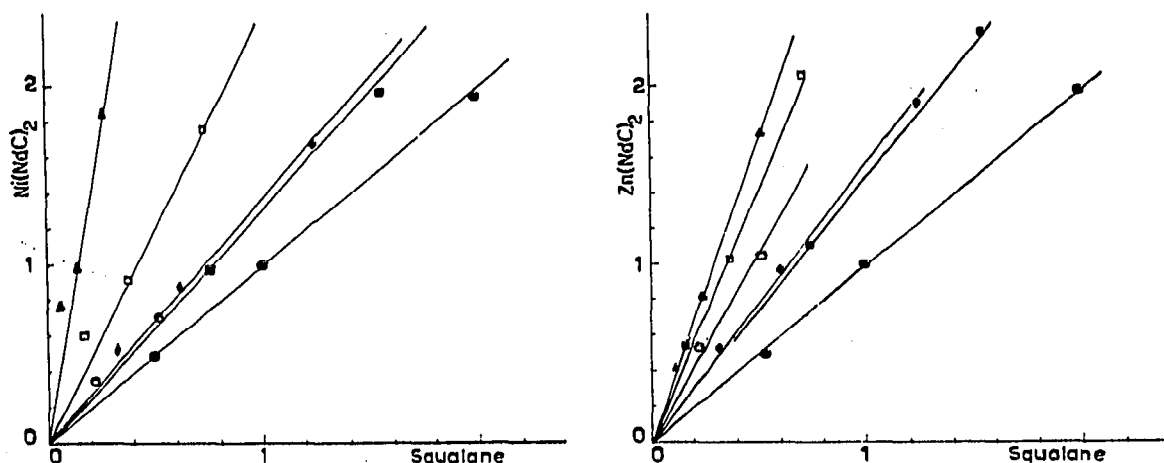


Fig. 1. Relative retention of homologous series of organic compounds upon a $Zn(NdC)_2$ column, a $Ni(NdC)_2$ column and a squalane column. (●) Alkanes; (■) aromatic hydrocarbons; (◆) ketones; (▲) primary alcohols; (□) secondary alcohols; (○) tertiary alcohols.

From the value of the specific retention volume, thermodynamic data related to the chromatographic process may be calculated and compared with those obtained with the squalane column. In Table IV the differences between the free energy of solution for various metal complexes $Me(NdC)_n$ and squalane (Sq) are reported ($\Delta G_{Me(NdC)_n} - \Delta G_{Sq}$).

The interaction of the various homologous series and the metal complexes is not very noticeable for the alkanes, aromatic hydrocarbons and ketones. The higher values measured for the alkanes should be related to their higher solubility in squalane, which is a compound of similar nature.

TABLE IV

DIFFERENCES (kcal) OF ΔG FOR $Me(NdC)_2$ AND SQUALANE COLUMNS AT 120°

	$Cu(NdC)_2$	$Ni(NdC)_2$	$Al(NdC)_3$	$Be(NdC)_3$	$Zn(NdC)_2$
Alkanes	$C_7 + 0.22$	+ 0.38	+ 0.18	+ 0.19	+ 0.36
Aromatic hydrocarbons	$C_6 - 0.17$	+ 0.15	- 0.16	- 0.20	+ 0.02
Ketones	$C_5 - 0.14$	+ 0.11	- 0.13	- 0.24	- 0.04
Tertiary alcohols	$C_5 - 0.17$	+ 0.15	- 0.05	- 0.17	- 0.18
Secondary alcohols	$C_4 - 0.28$	- 0.42	- 0.27	- 0.35	- 0.43
Primary alcohols	$C_4 - 0.46$	- 1.17	- 0.45	- 0.62	- 0.59

The interaction of the alcohols with metal complexes is very large and these phases can be considered selective for the determination of these compounds. The alcohols should be regarded as effective ligands for complex formation with metal diketones. The complexing action increases from the tertiary to the primary alcohols and is quite effective in the case of zinc and beryllium and more pronounced for nickel. Very likely the high value of interaction between the nickel complex and primary alcohols (- 1.17 kcal) should be attributed to structural change of the nickel complex.

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SUMMARY

Complexes of *n*-nonyl- β -diketones with copper, nickel, aluminium, beryllium and zinc have been prepared and used as liquid phases in packed columns (20 % on celite) for gas chromatography. They have a rather low melting point and a low vapour pressure.

A series of retention volumes have been measured for homologous series of various compounds (alkanes, aromatic hydrocarbons, ketones, and alcohols) and these values have been compared with the retention volumes obtained on a conventional squalane column. The differences of thermodynamic functions have been determined and the retardation effect taken as a measurement of the interaction between the various compounds and the metal complexes. Particularly strong interaction has been found between the alcohols (especially the primary) and the *n*-nonyl- β -diketone nickel complex.

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