

Note

Gas chromatographic analyses of hydroxyoxime extractants of metals and their intermediates

I. Alkylsalicylaldehyde oximes

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Alkyl derivatives of salicylaldehyde oximes, produced by Acorga (Acorga P-50) and Henkel (LIX 860), are some of the most important copper extractants, used in some old and new plants^{1–4}. According to the manufacturers, Acorga P 50 contains 2-hydroxy-5-nonylbenzaldehyde oxime and LIX 860 contains 2-hydroxy-5-dodecylbenzaldehyde oxime. The Acorga reagents Acorga P-5100, P-5200 and P-5300 are blends of P-50 and nonylphenol with weight ratios of 1:1, 1:2 and 1:3, respectively, and Acorga PT-5050 is a 2:1 blend of P-50 and tridecanol. Apart from LIX 860, Henkel reagents containing 2-hydroxy-5-dodecylbenzaldehyde oxime are LIX 622, a mixture of LIX 860 and tridecanol, LIX 984, a 1:1 blend of LIX 860 and LIX 84 (2-hydroxy-5-nonylacetophenone oxime), and LIX 865, a mixture of LIX 860 and LIX 65N (2-hydroxy-5-nonylbenzophenone oxime).

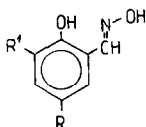
These extraction reagents are diluted to approximately 50% with aliphatic–aromatic solvents. The disadvantage of the alkyl derivatives of salicylaldehyde oximes is a faster hydrolysis to aldehydes in strongly acidic conditions in relation to standard LIX 65N. As a result, appropriate aldehydes can be present in commercial products and they can be formed during extraction⁵.

2-Hydroxy-5-alkylbenzaldehyde oximes have not been analysed by gas chromatography (GC). High-performance liquid chromatography (HPLC) has been used for the determination of nonylphenol, aldehydes and oximes in the commercial Acorga series P-5000⁶. GC and/or HPLC have been used for the identification and determination of other aliphatic α -hydroxyoximes (LIX 63) and some aromatic β -hydroxyoximes (all of the above 2-hydroxybenzophenone derivatives)^{7–10}.

The aim of this work was to obtain some analytical data for model and commercial hydroxyoxime metal extractants (alkyl derivatives of salicylaldehyde oxime) on some different phases, to investigate the relationships between the arithmetic retention indices of these compounds and their structures and to calculate increments of the retention indices for some characteristic groups present in these compounds.

EXPERIMENTAL

Individual model derivatives of salicylaldehyde oxime¹¹ of the following structure:



where R denotes H, methyl ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-dodecyl, *tert.*-butyl and 1,1,3,3-tetramethylbutyl, (*tert.*-octyl) and R¹ denotes H, Cl, *tert.*-butyl and NO₂ were analysed in the form of trimethylsilyl derivatives. Two commercial extractants, Acorga P 5100 and P 5300, were also analysed.

A sample of 10–20 mg was treated with 0.2 cm³ of N,O-bis(trimethylsilyl)acetamide (BSA) or N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 50°C for 30 min.

Gas chromatographic analyses were carried out with a JEOL Model JGC 1100 TFP instrument equipped with a flame ionization detector. The glass columns were filled with 3% SE-30 on Gas-Chrom Q (100–120 mesh) (column I), 3% OV-210 on Gas-Chrom Q (120–140 mesh) (column II) or 3% OV-225 on Gas-Chrom Q (120–140 mesh) (column III). Column I was 2 m long and columns II and III 1.8 m long, each of I.D. 3 mm. Helium was used as the carrier gas at a flow-rate of 40 cm³/min. The injector and detector temperatures were 290°C. The oven temperature was increased linearly at 4°C/min from 80 to 280°C for column I and from 50 to 250°C for columns II and III.

Silylated samples of 0.1-μl volume were injected and the arithmetic retention indices were calculated using C₁₀–C₂₄, C₂₆, C₂₈ and C₃₂ *n*-alkanes as reference standards. In those instances when a compound in the sample was not separated or was separated incompletely from an *n*-alkane, this standard was omitted from the mixture and its retention time was calculated from its relative retention time in another mixture.

Commercial extractants were analysed using column I. The weight ratio of nonylphenol to 2-hydroxy-5-nonylbenzaldehyde oxime was determined from peak surface areas assuming correction coefficients to be equal to 1. The peaks of 2-hydroxy-5-alkylbenzaldehyde oxime and nonylphenol in commercial Acorga extractants were identified by comparison with chromatograms of nonylphenol and the hydroxyoxime obtained from intermediate nonylphenol.

RESULTS AND DISCUSSION

Derivatives of salicylaldehyde oximes have two active groups *i.e.*, a hydroxyl phenolic group and an oximino group. Each of these two groups can react with a silylation agent to form appropriate trimethylsilyl derivatives:

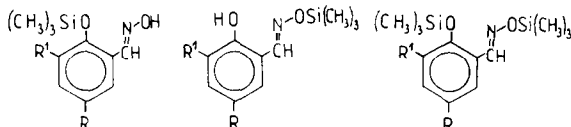


TABLE I

INFLUENCE OF DIFFERENT TEMPERATURE PROGRAMMES ON ARITHMETIC RETENTION INDICES ON SE-30

Maximum standard deviation = 0.3

Compound	Temperature programme [starting temperature (°C) rate of increase (°C/min)]			
	50/6	60/4	80/4	100/3
2,4-Di- <i>tert.</i> -butylphenol	1539.6	1538.3	1538.7	1537.6
4- <i>tert.</i> -Octylphenol	1630.9	1628.7	1629.2	1628.1
2-Hydroxy-5- <i>tert.</i> -butylbenzaldehyde oxime	1762.4	1763.3	1763.1	1763.3
2-Hydroxy-5- <i>tert.</i> -butylbenzaldehyde	1881.9	1877.6	1878.6	1875.5
2-Hydroxy-3,5-di- <i>tert.</i> - butylbenzaldehyde oxime	1936.6	1936.2	1936.7	1936.1
2-Hydroxy-3-chloro-5- <i>tert.</i> - octylbenzaldehyde oxime	2106.9	2104.5	2104.7	2102.9

As a result, three peaks may be observed on chromatograms. However, under the experimental conditions used for silylation (after a reaction time of 30 min), only one peak of the appropriate di(trimethylsilyl) derivative was observed and its size and shape did not change after further silylation. The structure of the di(trimethylsilyl) derivative was confirmed by gas chromatography-mass spectrometry.

The effect of various temperature programmes on the arithmetic retention index for the compounds considered is small and can be neglected (Table I). The maximum standard deviation is 0.3.

The determined values of the arithmetic retention index are given in Table II, and the relationships between retention indices determined on OV-210 and OV-225

TABLE II

VALUES OF ARITHMETIC RETENTION INDICES

Group		Stationary phase		
<i>R</i>	<i>R</i> ¹	SE-30	OV-210	OV-225
H	H	1560	1739	1803
Methyl	H	1627	1793	1864
Ethyl	H	1693	1849	1925
<i>n</i> -Butyl	H	1852	2004	2081
<i>n</i> -Hexyl	H	2031	2185	2258
<i>n</i> -Octyl	H	2216	2369	2445
<i>n</i> -Dodecyl	H	2606	2745	2827
<i>tert.</i> -Butyl	H	1763	1909	1966
<i>tert.</i> -Butyl	<i>tert.</i> -Butyl	1937	2013	2051
<i>tert.</i> -Butyl	Cl	1873	2026	2066
<i>tert.</i> -Octyl	H	1995	2144	2171
<i>tert.</i> -Octyl	Cl	2105	2267	2271
<i>tert.</i> -Octyl	NO ₂	2241	2671	2606

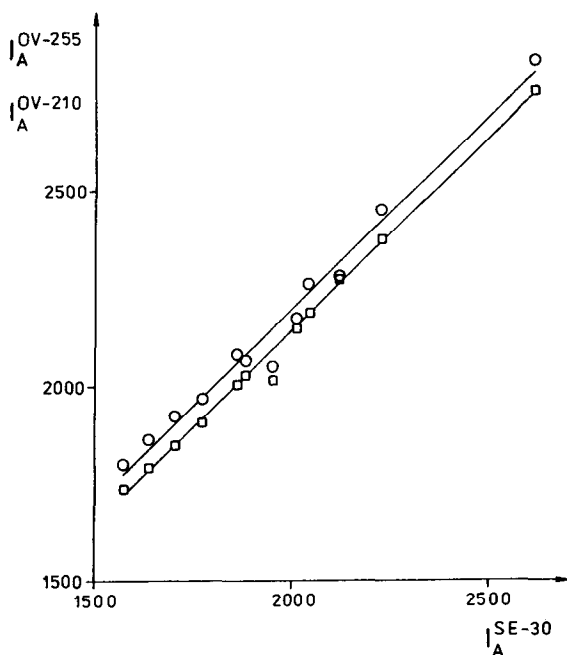


Fig. 1. Relationship between arithmetic retention indices on (□) OV-210 or (○) OV-225 and arithmetic retention indices on SE-30.

and those on SE-30 are presented in Fig. 1. The phases used for the analysis of both the commercial and model hydroxyoxime extractants were considered.

The retention indices of 2-hydroxy-5-alkylbenzaldehyde oximes on OV-210 and OV-225 are higher than those on the non-polar SE-30 by *ca.* 155 and 222 units, respectively. The following statistically significant linear relationships were obtained:

$$I_A^{OV-210} = 0.977I_A^{SE-30} + 194 \quad R^2 = 0.9926$$

$$I_A^{OV-225} = 0.978I_A^{SE-30} + 249 \quad R^2 = 0.9824$$

where R^2 is the determination coefficient (the square of the correlation coefficient).

Statistically significant linear relationships are also observed between the arithmetic retention indices of 2-hydroxy-5-*n*-alkylbenzaldehyde oximes and the number of carbon atoms (n) in the alkyl group. They are as follows on SE-30, OV-210 and OV-225, respectively:

$$I_A^{SE-30} = 94.5n + 1468 \quad R^2 = 0.9996$$

$$I_A^{OV-210} = 92.7n + 1631 \quad R^2 = 0.9999$$

and

$$I_A^{OV-225} = 93.5n + 1702 \quad R^2 = 0.9999$$

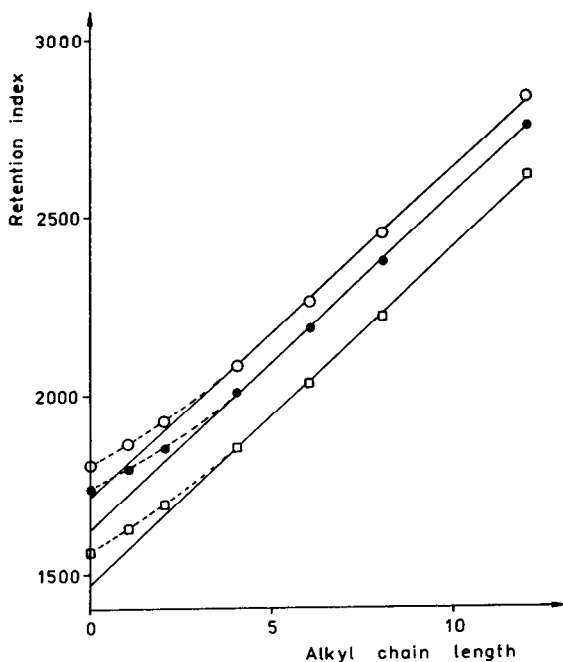


Fig. 2. Relationship between arithmetic retention indices of 2-hydroxy-5-*n*-alkylbenzaldehyde oximes on (□) SE-30, (●) OV-210 and (○) OV-225 and length of alkyl chain.

Hence, the determined increments of the methylene/methyl group (95, 93 and 94) are approximately the same and near to the theoretical value of 100.

Some important deviations from these linear relationships are observed for homologues having a short alkyl chain, *i.e.*, containing less than four carbon atoms (Fig. 2). These deviations increase as the length of the alkyl chain decreases, and they disappear for oximes with a butyl group.

The data in Table II also demonstrate that the chlorine atom at the 3-position, *i.e.*, in the direct neighbourhood of the phenolic group, increases the retention index by approximately 110, 120 and 100 units on SE-30, OV-210 and OV-225, respectively, and the effect of the alkyl chain length (*tert.*-butyl or *tert.*-octyl) is relatively small.

The presence of a *tert.*-butyl group at the 3-position increases the retention index by 174, 104 and 85 units on these three phases, respectively, while the replacement of an *n*-butyl group with a *tert.*-butyl group decreases the retention index by 84, 95 and 115 units, respectively. A much stronger effect is observed when the *n*-octyl group is replaced with a *tert.*-octyl group, which contains mainly 1,1,3,3-tetramethylbutyl; the retention index decreases by 221, 225 and 274 units on SE-30, OV-210 and OV-225, respectively.

A nitro group at the 3-position strongly increases the retention index by 246, 527 and 435 units, respectively.

A typical chromatogram of the commercial extractant Acorga P 5100 is given in Fig. 3. Two groups of components were separated which were identified as nonyl-phenol (arithmetic retention indices above 1700 with a range of about 70 units) and

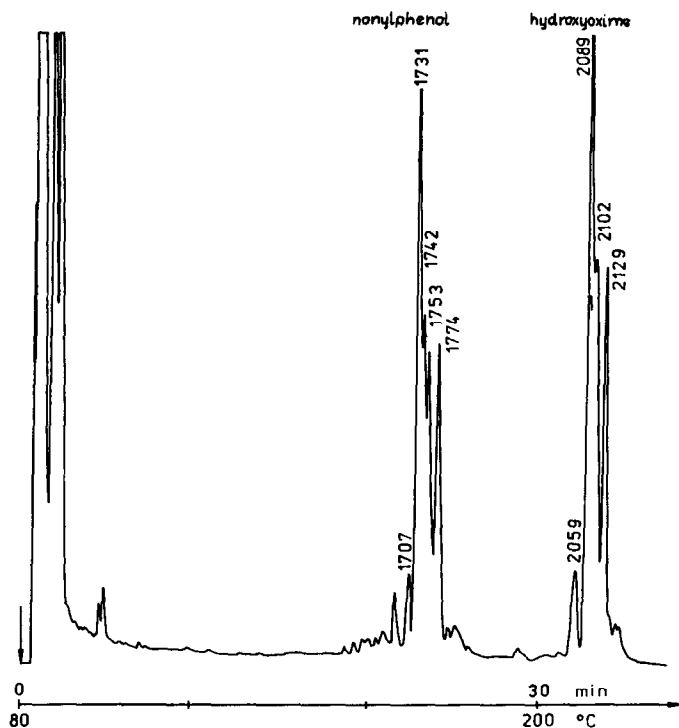


Fig. 3. Chromatogram of commercial extractant Acorga P 5100.

2-hydroxy-5-nonylbenzaldehyde oxime (arithmetic retention index of about 2100 with a range of 70 units).

The separation of several components is caused by the complex composition of the commercial nonylphenol obtained by phenol alkylation with propylene trimer. As a result, the nonyl group is highly branched and nonylphenol contains several iso-

TABLE III

WEIGHT RATIO OF NONYLPHENOL TO 2-HYDROXY-5-NONYLBENZALDEHYDE OXIME IN COMMERCIAL EXTRACTANTS P 5100 AND P 5300

Analysis No.	P 5100	P5300
1	0.88	3.10
2	0.98	3.31
3	0.87	2.82
4	0.98	2.92
5	0.89	2.82
6	0.94	3.30
7	0.93	2.93
Average	0.93	3.03

mers. Moreover, it also contains other groups of components, including 2-alkylphenol and small amounts of O-alkylation products¹².

The determined weight ratios of nonylphenol to 2-hydroxy-5-nonylbenzaldehyde in Acorga P 5100 and P 5300 (Table III) are in good agreement with the values given by manufacturer, *i.e.*, 1:1 and 3:1 in P 5100 and P5300, respectively.

CONCLUSIONS

Linear relationships are observed between retention indices on OV-210 and OV-225 and on SE-30 for 2-hydroxy-5-alkylbenzaldehyde oximes and their derivatives substituted at the 3-position. The retention indices of 2-hydroxy-5-*n*-alkylbenzaldehyde oximes increase linearly as the length of the alkyl group increases. Some deviations from linear relationships are observed only for the first homologues containing less than four carbon atoms in the alkyl group.

The increments of various structural groups present in the compounds considered can be used to estimate their retention indices on phases considered.

Chromatographic analyses confirm the weight ratio of nonylphenol to 2-hydroxy-5-nonylbenzaldehyde oxime in commercial extractants P 5100 and P 5300 as 1:1 and 3:1, respectively.

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REFERENCES

- 1 P. R. Danesi and R. Chiarizia, *CRC Crit. Rev. Anal. Chem.*, 10 (1980) 1–126.
- 2 J. F. C. Fisher and G. W. Notebart, in T. C. Lo, M. H. I. Baird and C. Hanson (Editors), *Handbook of Solvent Extraction*, Wiley, New York, 1983, pp. 649–665.
- 3 J. Szymanowski, *Wiad. Chem.*, 38 (1984) 371–399.
- 4 J. Szymanowski, in *Proceedings of the Annual Scientific Meeting of the Polish Chemical Society, Poznań, Poland*, Poznań University, Poznań, 1985, pp. 48–70.
- 5 R. J. Whewell, H. J. Foakes and M. A. Hughes, *Hydrometallurgy*, 7 (1981) 7–26.
- 6 I. C. Stone, T. N. Anderson, J. C. Parr and D. D. Metcalf, *Anal. Chem.*, 54 (1982) 1965–1968.
- 7 A. W. Ashbrook, *J. Chromatogr.*, 105 (1975) 151–156.
- 8 W. Sowa, B. H. Licht and I. J. Itzkovitch, *J. Chromatogr.*, 116 (1976) 197–200.
- 9 J. W. Hosking and N. M. Rice, *Hydrometallurgy*, 3 (1978) 217–231.
- 10 E. Y. O. Paatero, *Hydrometallurgy*, 13 (1984) 193–201.
- 11 D. Stepniak-Biniakiewicz and J. Szymanowski, *Hydrometallurgy*, 7 (1981) 299–313.
- 12 V. Gerhardt and H. Much, *Tenside Deterg.*, 18 (1981) 120–124.