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COORDINATION POLYMERS AS ADSORBENTS AND STATIONARY PHASES IN GAS CHROMATOGRAPHY

VI. SEPARATION PROPERTIES OF ALKALINE-EARTH METAL DI-*n*-HEXYLPHOSPHINATES

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SUMMARY

The separation properties of alkaline-earth metal di-*n*-hexylphosphinates in relation to hydrocarbons have been described. The possibilities of specific interactions of unsaturated hydrocarbons with alkaline-earth metals are noted. A number of chromatographic separations on magnesium di-*n*-hexylphosphinate are reported.

INTRODUCTION

Alkaline-earth metal compounds have rarely been used as stationary phases or adsorbents in gas chromatography (GC). BaCl₂ (refs. 1, 2) and BaSO₄ (ref. 3) have been studied more extensively; the application of halides of Sr and Ba as adsorbents has also undergone careful investigations⁴. CaCl₂ and other metal chlorides have been used for silica gel modification⁵, while a mixture of CaF₂ and CsF was employed for separation of fluorine compounds⁶. Zeolites of Mg, Ca, Sr and Ba⁷ has also been.

It seemed more interesting to find out the chromatographic properties of alkaline-earth metal di-*n*-hexylphosphinates (DHP) because DHP-Mg has already been shown to exhibit good separation properties^{8,9}. Thus, DHP-Ca, DHP-Sr and DHP-Ba have been synthesized, applied as adsorbents in GC and their separation properties compared for 22 C₆ hydrocarbons.

EXPERIMENTAL

Synthesis of phosphinates

DHP-Mg was synthesized as described previously⁸; DHP-Ca was obtained analogously.

DHP-Sr. A 5-g amount of di-*n*-hexylphosphinic acid¹⁰ was dissolved in 50 ml of methanol and neutralized with a stoichiometric amount of 1 *N* KOH. Water was added to give a total volume of 100 ml, and then 100 ml of chloroform. To this mixture, an aqueous solution of SrCl₂ (2.8448 g SrCl₂·6H₂O in 50 ml of water) was added

dropwise and the solution mixed continuously with a magnetic stirrer. The final solution was stirred for 24 h. The chloroform layer was separated, and the water layer was washed twice with 25 ml of chloroform. The combined chloroform layers were evaporated and a white precipitate of $\text{DHP-Sr} \cdot 1/2 \text{H}_2\text{O}$ was obtained. The compound was dehydrated by drying for 48 h in a vacuum above molecular sieves 4A and 5A.

DHP-Ba. A 5 g amount of di-*n*-hexylphosphinic acid was dissolved in 50 ml of methanol and neutralized with the stoichiometric amount of 1 N KOH. A gelatinous precipitate of DHP-Ba was obtained when BaCl_2 (2.609 g in 50 ml of water) was added to the solution. A 50-ml volume of water was added and the solution then evaporated to ca. 50 ml in volume. This procedure was repeated twice. Then, the precipitate was filtered off, rinsed well and dried, first at 100° and then above molecular sieves 4A and 5A in a vacuum for 48 h.

The phosphinates were identified by means of IR spectra and elemental analysis. The analyses results and some properties of the phosphinates are presented in Table I.

Porasil C DMCS was coated with phosphinates so that each surface concentration was 10^{-4} mole of phosphinate per gram of adsorbent. Therefore 5% DHP-Mg, 5.16% DHP-Ca, 5.64% DHP-Sr and 6.15% DHP-Ba were precipitated on the support. These packings were conditioned at 150° in a stream of Ar for 15 h. Stainless-steel columns (1 m × 4 mm) were used. Some separations were carried out with the help of a steel micropacked column (1.5 m × 0.8 mm). The particle size of each packings was 0.10–0.12 mm.

TABLE I

ELEMENTAL ANALYSIS AND SOME PROPERTIES OF ALKALINE-EARTH METAL DI-*n*-HEXYLPHOSPHINATES

Phosphinate	Analysis (%) ^a			M.p. (°C)	Decomposition temp. (°C)	Colour
	C	H	M			
DHP-Mg	58.72	10.68	4.96	100	300	white
	58.70	10.64	4.62			
DHP-Ca	56.89	10.35	7.89	107–108	330	white
	56.68	10.29	7.62			
DHP-Sr	52.01	9.45	15.80	108–109	330	white
	52.00	9.33	15.53			
DHP-Ba	47.74	8.51	23.07	109–110	330	white
	47.52	8.24	23.14			

^a Calculated followed by found values.

Decomposition temperatures of phosphinates were obtained with the aid of a Paulik, Paulik, Erdey Derivatograph (MOM, Budapest, Hungary). A Böetius microscopic table was used to determine the melting points.

RESULTS AND DISCUSSION

Retention times and volumes were measured for 22 C_6 hydrocarbons on all of the packings at four temperatures ranging from 70 to 90°. The k' values for the columns of alkaline-earth metal di-*n*-hexylphosphinates are collected in Table II.

TABLE II

CAPACITY RATIO k' FOR COLUMNS CONTAINING ALKALINE-EARTH METAL DI- π -HEXYLPHOSPHINATES AT 70°

Compound	k'			
	DHP-Mg	DHP-Ca	DHP-Sr	DHP-Ba
Pentane	1.48	1.32	1.34	1.35
Heptane	6.03	5.56	5.82	5.49
Octane	12.19	11.41	12.25	11.09
Hexane	2.94	2.72	2.79	2.73
1-Hexene	2.93	2.58	2.73	2.65
1-Hexyne	4.25	3.44	3.98	3.71
1,5-Hexadiene	2.84	2.45	2.64	2.55
2,4-Hexadiene	5.89	4.43	5.08	4.83
<i>cis</i> -2-Hexene	3.50	2.95	3.22	3.08
<i>trans</i> -2-Hexene	3.31	2.82	3.01	2.91
<i>cis</i> -3-Hexene	3.23	2.80	3.02	2.91
<i>trans</i> -3-Hexene	3.20	2.78	2.97	2.87
Cyclohexane	4.53	3.51	4.02	3.92
Cyclohexene	5.66	4.02	4.84	4.63
1,3-Cyclohexadiene	6.00	4.03	4.92	4.68
1,4-Cyclohexadiene	7.95	5.10	6.37	6.01
Benzene	6.64	4.21	5.65	4.97
3-Methylpentane	2.70	2.46	2.55	2.48
3-Methylpentene-1	2.37	2.15	2.26	2.19
<i>cis</i> -3-Methylpentene-2	3.39	2.89	3.18	3.04
<i>trans</i> -3-Methylpentene-2	3.61	3.07	3.35	3.23
Methylcyclopentane	3.56	2.91	3.20	3.14
2-Methylpentene-1	2.89	2.57	2.77	2.67
4-Methylpentene-1	2.34	2.17	2.26	2.20
<i>trans</i> -4-Methylpentene-2	2.58	2.33	2.45	2.38

The highest k' values and the biggest differences between individual compounds have been observed for the column containing DHP-Mg. This column, then, can be expected to show the best separation properties. It is interesting to compare phosphinate separation properties for *cis* and *trans* isomers (Table III).

TABLE III

COMPARISON OF THE SEPARATION PROPERTIES OF PHOSPHINATES AND SOME LIQUID STATIONARY PHASES IN RELATION TO *cis* AND *trans* ISOMERS

Values are of $\alpha = cis/trans$. ODPN = β, β' -oxydipropionitrile (2.5-m column); DMS = dimethylsulpholane (2.5-m column); TCP = tricresylphosphate (2.5-m column); SQ = squalane (600-ft. column).

Compound	DHP-Mg 70°	DHP-Ca 70°	DHP-Sr 70°	DHP-Ba 70°	ODPN* 27°	DMS* 27°	TCP* 27°	SQ* 49°
2-Hexene	1.060	1.047	1.070	1.061	1.22	1.13	1.11	1.07
3-Hexene	1.009	1.008	1.017	1.014	1.16	1.05	0.98	1.00
3-Methylpentene-2	0.939	0.943	0.950	0.942	0.94	0.90	0.89	0.90

Of the columns studied here. DHP-Sr gave the best separation of *Cis* and *trans* isomers of *n*-hydrocarbons, but branched hydrocarbon, were best separated on DHP-Mg. It is worthy of note that *trans*-3-methylpentene-2 is eluted later than the corresponding *cis*-isomer regardless of the lower boiling point of the *trans*-form. The retention index of the *cis* isomer on squalane is also lower than that of *trans*-isomer^{11,12}. A similar case has been previously described¹³, and *trans*-4-methylpentene-2 shows a higher stability constant with PdCl₂ than the corresponding *cis*-isomer. Phosphinate phases show little of the selectivity of liquid phases; it must be remembered, however, that the phosphinate data were obtained at a higher temperature.

Hively¹⁴ suggests that the terms *cis* and *trans* in relation to such compounds as 3-methylpentene-2, 3-methylhexe-3 and 3-methylhexene-2 should be reversed, so that the *trans*-isomer becomes the compound of higher boiling temperature, as verified by Cornforth *et al.*¹⁵. From the point of view of possible specific interactions between a metal and a multiple bond, it seems that a form with a lower boiling point



might cause stronger interactions than a form having a higher boiling point



due to obvious, smaller steric hindrance ($\text{CH}_3 < \text{C}_2\text{H}_5$). Such an interpretation also explains the reversed order of elution of *cis*- and *trans*-3-methylpentene-2 on phosphinates.

Table IV presents specific ${}^{\text{RT}}V_g$ and relative (*r*) retention volumes of hydrocarbons corresponding to 10^{-4} mole of phosphinate, *e.g.* to *ca.* 1 g of adsorbent. The ${}^{\text{RT}}V_g$ values are similar for all of the phosphinates. The relative retention volumes have been considered for three groups of sorbztes:

n-Hydrocarbons. The highest values may be observed on DHP-Sr and DHP-Mg. They are very approximate. Lower values were found on DHP-Ba and the lowest on DHP-Ca.

Cyclic hydrocarbons. The highest values and the best separation properties were observed on DHP-Mg, then DHP-Sr and DHP-Ba respectively and the lowest on DHP-Ca.

3-Methylpentane derivatives. The results were similar to those for cyclic hydrocarbons.

It may be concluded that the best separation properties (in relation to *n*-hydrocarbons) are expected on the column containing DHP-Mg. Relative retention volumes of unsaturated hydrocarbons show that usually these compounds are more strongly

TABLE IV
SPECIFIC AND RELATIVE RETENTION VOLUMES OF C₆ HYDROCARBONS

Compound	$^{RT}V_g$ (ml/g)				r			
	DHP-Mg	DHF-Ca	DHP-Sr	DHP-Ba	DHP-Mg	DHP-Ca	DHP-Sr	DHP-Ba
Pentane	2.403	2.648	2.289	2.623				
Heptane	9.813	11.130	9.952	10.669				
Octane	19.847	22.840	20.955	21.538				
Hexane	4.87	5.437	4.765	5.303	1.000	1.000	1.000	1.000
1-Hexene	4.765	5.163	4.674	5.152	0.978	0.950	0.981	0.972
1-Hexyne	6.927	6.882	6.815	7.208	1.422	1.266	1.430	1.359
1,5-Hexadiene	4.627	4.911	4.514	4.955	0.950	0.903	0.947	0.934
2,4-Hexadien	9.588	8.873	8.694	9.376	1.968	1.632	1.825	1.768
<i>cis</i> -2-Hexene	5.704	5.902	5.506	5.957	1.171	1.086	1.156	1.130
<i>trans</i> -2-Hexene	5.383	5.637	5.145	5.647	1.105	1.037	1.080	1.065
<i>cis</i> -3-Hexene	5.253	5.599	5.171	5.655	1.078	1.030	1.085	1.066
<i>trans</i> -3-Hexene	5.206	5.556	5.084	5.576	1.069	1.022	1.067	1.051
Cyclohexene	7.374	7.028	6.876	7.613	1.000	1.000	1.000	1.000
Cyclohexene	9.218	8.040	8.277	8.998	1.250	1.144	1.204	1.182
1,3-Cyclohexadiene	9.771	8.063	8.412	9.085	1.325	1.147	1.223	1.193
1,4-Cyclohexadiene	12.950	10.213	10.904	11.676	1.756	1.453	1.586	1.534
Benzene	10.814	8.428	9.656	9.665	1.466	1.199	1.404	1.269
3-Methylpentane	4.389	4.916	4.361	4.822	1.000	1.000	1.000	1.000
3-Methylpentene-1	3.860	4.309	3.859	4.257	0.879	0.876	0.885	0.883
<i>cis</i> -3-Methylpentene-2	5.524	5.793	5.446	5.907	1.258	1.178	1.249	1.225
<i>trans</i> -3-Methylpentene-2	5.884	6.141	5.732	6.272	1.341	1.249	1.314	1.301
Methylcyclopentane	5.792	5.828	5.480	6.101				
2-Methylpentene-1	4.708	5.148	4.743	5.187				
4-Methylpentene-1	3.806	4.335	3.864	4.277				
<i>trans</i> -4-Methylpentene-2	4.203	4.668	4.194	4.625				

retained than the respective alkanes. Hydrocarbons possessing higher unsaturation, e.g., 1-hexyne and dienes, usually have higher relative retention volumes than their respective alkenes. At the same time, 1-hexene and 1,5-hexadiene have relative (with respect to hexane) retention volumes lower than 1.

This does not mean that these compounds do not have specific interaction with phosphinates. The specific interactions of alkaline-earth metal ions with hydrocarbons will be discussed elsewhere.

Application of DHP-Mg to chromatographic separations

Since the retention data show that DHP-Mg packings exhibit the best separation properties, have applied this phase to the separation of model mixtures. Two

types of columns were used for chromatographic separations: classic and micropacked.

In gas chromatography DHP-Mg can be used in two ways: as an adsorbent, below the melting point; or as a liquid stationary phase, above the melting point⁹. Fig. 1 shows the separation on DHP-Mg, below its melting point, of several hydrocarbons of similar structure and properties, including three isomers. A similar separation of these compounds on squalane requires *ca.* 14 min on a micropacked column¹⁷. Fig. 2 shows a separation of several cyclic hydrocarbons.

DHP-Mg applications are not limited to hydrocarbons. Particularly interesting separation properties are shown by DHP-Mg above its melting point. Figs. 3-6 show separations of homologous series of compounds.

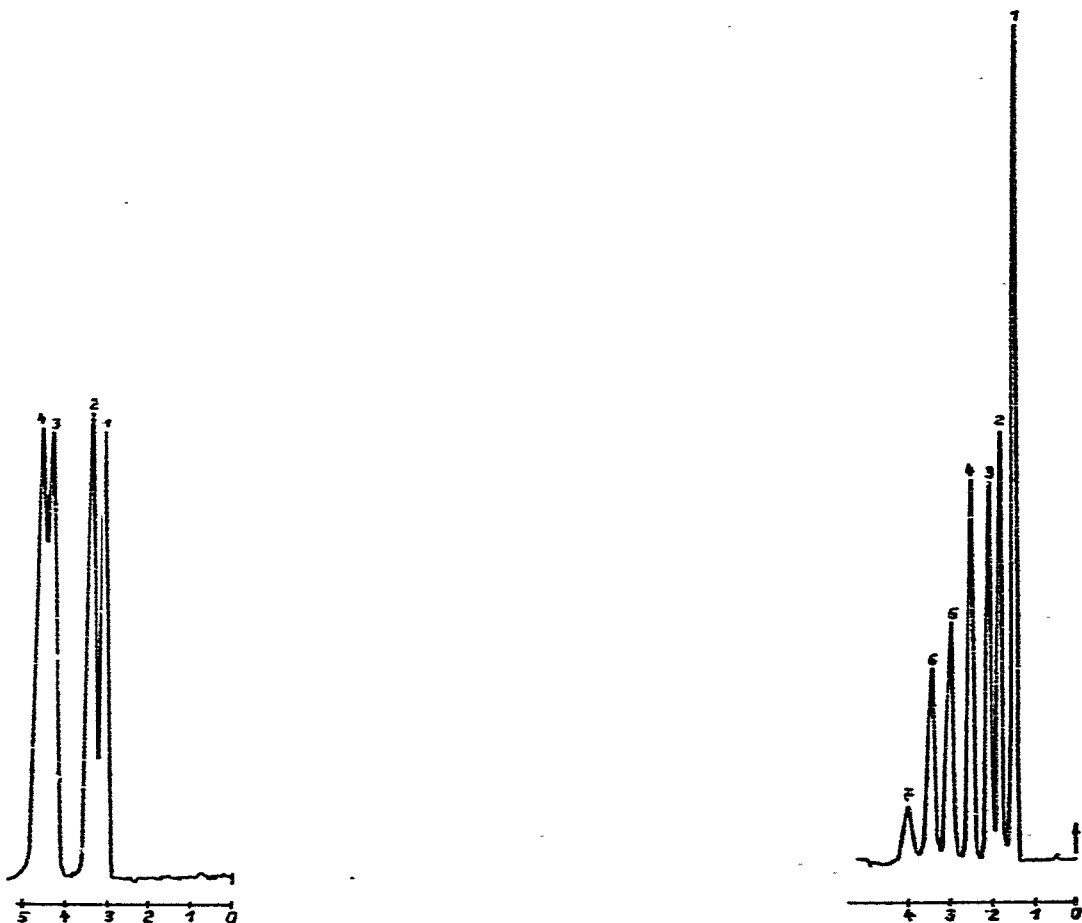


Fig. 1. Separation of some C_5 hydrocarbons. Peaks: 1 = 3-methylpentene-1; 2 = 3-methylpentane; 3 = *cis*-3-methylpentene-2; 4 = *trans*-3-methylpentene-2. Column: 1 m \times 4 mm I.D., packed with 5% DHP-Mg on Porasil C DMCS; $T_k = 59^\circ$; flow-rate of argon, $F_0 = 17.9$ ml/min.

Fig. 2. Analysis of some cyclic hydrocarbons. Peaks: 1 = cyclopentene; 2 = hexane; 3 = methylcyclopentane; 4 = cyclohexane; 5 = cyclohexene; 6 = benzene; 7 = 1,4-cyclohexadiene. Column as in Fig. 1; $T_k = 72^\circ$; $F_0 = 27.2$ ml/min.

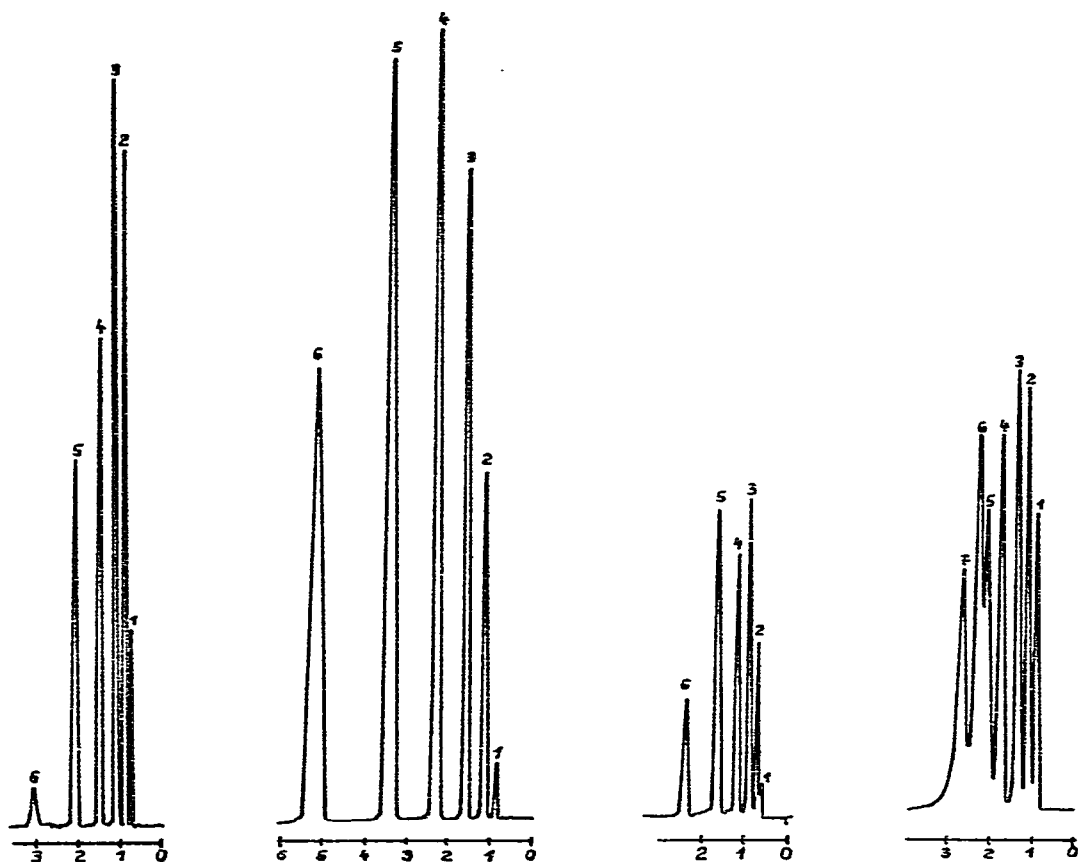


Fig. 3. Separation of C_5 - C_{10} . Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane. Column as in Fig. 1; $T_k = 129^\circ$; $F_0 = 26.6$ ml/min.

Fig. 4. Separation of 1-chloroalkanes. Peaks: 1 = 1-chloropentane; 2 = 1-chlorohexane; 3 = 1-chloroheptane; 4 = 1-chlorooctane; 5 = 1-chlorononane; 6 = 1-chlorodecane. Column: 1.5 m \times 0.8 mm I.D., packed with 5% DHP-Mg on Porasil C DMCS; $T_k = 137^\circ$; $F_0 = 4.5$ ml/min.

Fig. 5. Separation of aldehydes. Peaks: 1 = propanal; 2 = butanal; 3 = pentanal; 4 = hexanal; 5 = heptanal; 6 = octanal. Column as in Fig. 4; $T_k = 131.2^\circ$; $F_0 = 4.3$ ml/min.

Fig. 6. Separation of esters of acrylic and methacrylic acids. Peaks: 1 = methyl acrylate; 2 = methyl methacrylate; 3 = ethyl methacrylate; 4 = isobutyl acrylate; 5 = *sec.*-butyl methacrylate; 6 = isobutyl methacrylate; 7 = *n*-butyl methacrylate. Column as in Fig. 4; $T_k = 124.2^\circ$; $F_0 = 5.5$ ml/min.

Other interesting examples of the application of DAP-Mg are the separations of halogen derivatives of ethane and analysis of cichlorobenzene isomers, which requires only *ca.* 12 min, while in the case of a 18-m micropacked column containing liquid crystals such an analysis takes *ca.* 16 min¹⁸, with other phases much longer¹⁹. Only a mixture of silicone oil SP-1200 and Bentone 34 enables a faster separation of these isomers²⁰.

Finally, Figs. 9 and 10 show the separation of aromatic hydrocarbons.

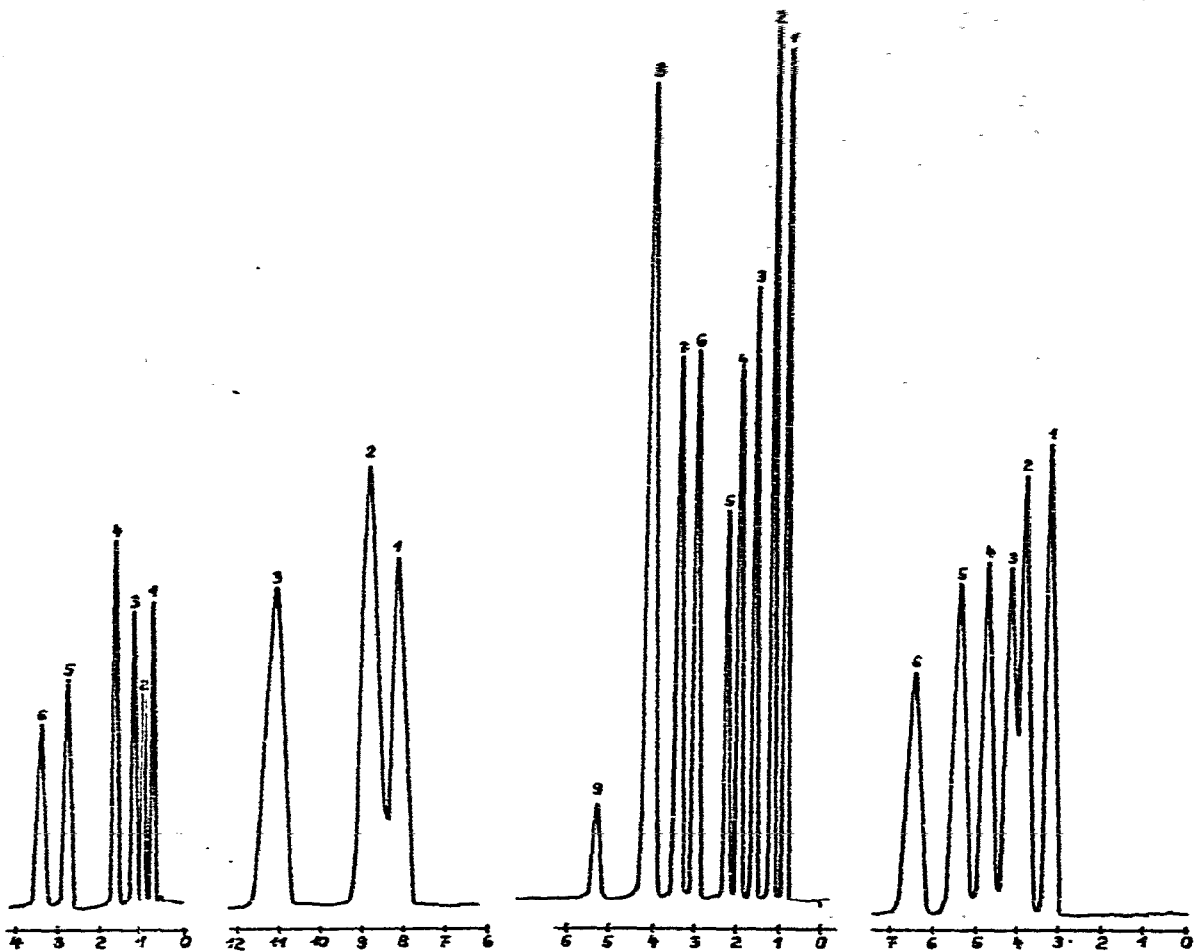


Fig. 7. Analysis of chloroethane derivatives. Peaks: 1 = chloroethane; 2 = 1,1-dichloroethane; 3 = 1,2-dichloroethane; 4 = 1,1,2-trichloroethane; 5 = 1,1,2,2-tetrachloroethane; 6 = pentachloroethane. Column as in Fig. 1; $T_k = 130.6^\circ$; $F_0 = 20.3$ ml/min.

Fig. 8. Separation of dichlorobenzenes. Peaks: 1 = *para*-; 2 = *meta*-; 3 = *ortho*-. Column as in Fig. 4; $T_k = 107^\circ$, $F_0 = 4.4$ ml/min.

Fig. 9. Separation of aromatic hydrocarbons. Peaks: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = styrene; 5 = *n*-propylbenzene; 6 = *p*-cymene; 7 = *n*-butylbenzene; 8 = *sec.*-pentylbenzene; 9 = *p*-diisopropylbenzene. Column as in Fig. 4; $T_k = 129.4^\circ$; $F_0 = 6.02$ ml/min.

Fig. 10. Separation of aromatic C_9 isomers. Peaks: 1 = isopropylbenzene; 2 = *n*-propylbenzene; 3 = 3-ethyltoluene; 4 = 1,3,5-; 5 = 1,2,4-; 6 = 1,2,3-trimethylbenzene. Column as in Fig. 4; $T_k = 101.6^\circ$, $F_0 = 5.6$ ml/min.

CONCLUSIONS

We have confirmed the good separation properties of phosphonates that have been described before²¹. Retention data indicate the existence of specific interactions between alkaline-earth metal atoms and unsaturated hydrocarbons. Our next paper will be concerned with a quantitative evaluation of these interactions.

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