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Gas chromatographic separation of unsaturated polar compounds on inorganic stationary phases containing silver nitrate

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ABSTRACT

    The separation of unsaturated compounds using gas chromatographic packed columns with inorganic liquid stationary phases was studied. Steam of steam–nitrogen was used as the mobile phase. Comparison of the retention characteristic for olefinic hydrocarbons and polar unsaturated compounds with $AgNO_3$ and $LiNO_3$ as stationary phases was carried out. Examples of separations on other nitrates are presented.

INTRODUCTION

    Glycol solution containing silver salts (usually silver nitrate) is one of the most selective liquid phases used to separate complex mixtures of olefinic hydrocarbon isomers. However, the use of this type of phase is limited by the poor stability at high temperatures [1,2]. Previously, we have shown [3] that the simultaneous application of steam as a carrier gas and some inorganic salts coated on a solid support as a liquid stationary phase led to the formation of salt solutions with unique chromatographic properties. Phases of this type were found to be characterized by very high selectivity with respect to oxy compounds (*e.g.*, alcohols) and unsaturated compounds if use is made of silver salts. The thermal stability of inorganic silver-containing phases permits stereoisomers of olefinic hydrocarbons up to C_{16} to be separate.
    The aims of this work were as follows: (1) to study the selective separations obtained with inert gas containing steam at concentrations corresponding to water vapour saturation at 60 and 25°C as the carrier gas; (2) further evaluation of the chromatographic characteristics of mixed phases containing $AgNO_3$ and another nitrate in chromatography with steam as the carrier gas; and (3) investigation of the possibility of using stationary phases with $AgNO_3$ for the separation of both olefins and other classes of polar saturated and unsaturated compounds.

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EXPERIMENTAL

Separations of C_1–C_5 aliphatic alcohols, C_{10}–C_{16} unsaturated hydrocarbons, some unsaturated alcohols and ethers was studied. Water–salt phases formed in the interaction steam of with either pure salt or salt mixtures were used as stationary phases. In the latter instance $AgNO_3$ was used as one of the components of the mixture.

The gas chromatographic system, described in detail previously [4], consists of a gas chromatograph equipped with a stem generator. The sorbent is prepared by deposition of an inorganic salt or salt mixture from an aqueous solution in amount of 5 or 10% (w/w) on Chromaton N AW (Lachema, Brno, Czechoslovakia) or 20% (w/w) on Celite C-22 (Ferak, Berlin, Germany). The column dimensions were 2 m × 3 mm I.D. When pure steam was used as the carrier gas, the column temperature was 108°C and the inlet vapour pressure 1.2–1.3 atm. The linear velocity of the carrier gas (nitrogen) was 4 cm/s. To saturate the inert gas while working with steam an inert gas mixture bubbler was used. The saturation temperature was 25 or 60°C. According to reference data, the water saturation pressure at these temperature is 23.7 and 150 Torr, respectively. The temperature of the column packed with $AgNO_3$ on Celite C-22 (nitrogen–steam mixed mobile phase) was 80°C. To ascertain whether a homo-genous liquid phase (aqueous salt solution) was formed with the salt mixture direct visual observation of the physical state of the salt was carried out in a test-tube at temperatures typical of chromatography with steam and steam–nitrogen mixtures.

RESULTS AND DISCUSSION

Retention data for some organic compounds are given in Tables I–IV. It is interesting that even $LiNO_3$ can be used to separate olefinic isomers although it is inferior to $AgNO_3$ in this respect. An increase in the salt content leads to an increase in retention and improves the separation. It should be mentioned that the elution trends are the same as with $AgNO_3$, *i.e.* the *trans* isomer is eluted before the *cis* isomer (Table I).

The molecular mass, ester structure and polar group position affect the reten-tion of unsaturated esters on $LiNO_3$ (Table II). Thus allyl formate (b.p. 83.6°C) elutes last although its boiling point is close to that of ethyl acrylate (80.3°C), which elutes earlier (relative retentions 1.5 and 0.56, respectively). The following retention *vs.* polarity dependence is observed: on $AgNO_3$ ethyl acrylate elutes first whereas on $LiNO_3$ allylethyl ether (b.p. 67.6°C) elutes first.

An extremely strong retention of unsaturated alcohols compared with that of aliphatic alcohols is typical for both $LiNO_3$ and $AgNO_3$, although the nature of the retention differs considerably. An increase in lithium salt content leads to a sharper increase in the retention of cinnamyl alcohol compared with allyl alcohol. In the presence of $AgNO_3$, the elution of allyl alcohol is retarded compared with cinnamyl alcohol.

With aliphatic alcohols, the retention is stronger with $LiNO_3$, but $AgNO_3$ shows the ability to separate aliphatic alcohols with respect to its polarity and not molecular mass.

The fact that lithium salts show a stronger retention with respect to unsaturated

TABLE I

CAPACITY FACTORS (k') AND RELATIVE RETENTION TIMES $(t_{rel})^a$ FOR UNSATURATED HYDRO-
CARBONS WITH $LiNO_3$ and $AgNO_3$

Carrier gas, steam; temperature, 108°C; column 200 × 3 mm I.D.

Compounds	Dry salt on solid support											
	$LiNO_3$				$AgNO_3$				$LiNO_3 + AgNO_3$			
	5%		10%		5%		10%		2% + 2%		5% + 5%	
	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}
trans-5-Decene	0.28	0.22	0.28	0.13	0.60	0.18	0.59	0.16	0.76	0.33	0.60	0.17
1-Decene	0.37	0.22	0.37	0.17	0.71	0.22	0.71	0.19	0.78	0.34	0.72	0.21
cis-5-Decene	0.35	0.27	0.51	0.24	0.83	0.26	0.84	0.23	0.82	0.36	0.85	0.25
trans-6-Dodecene	0.45	0.35	0.66	0.31	0.95	0.29	0.99	0.27	0.86	0.38	0.96	0.28
1-Dodecene	0.55	0.42	0.86	0.40	1.05	0.32	1.26	0.34	0.91	0.40	1.12	0.33
cis-6-Dodecene	0.66	0.51	1.14	0.53	1.22	0.38	1.45	0.40	0.97	0.43	1.32	0.38
trans-5-Tridecene	0.80	0.62	1.42	0.66	1.50	0.46	1.66	0.45	1.09	0.48	1.67	0.48
cis-5-Tridecene	1.02	0.78	1.73	0.80	1.85	0.57	2.09	0.57	1.26	0.55	1.93	0.56
1-Tetradecene	1.30	1.00	2.16	1.00	3.25	1.00	3.66	1.00	2.28	1.00	3.45	1.00
1-Cetene	2.18	1.68	4.59	2.125	6.75	2.08	9.66	2.64	3.50	1.54	6.78	1.97

^{a} Internal standard, ethyl vinylacetate.

polar compounds than to aliphatic compounds was used to develop a procedure for
the analysis of impurities (ethyl acetate and butyl acetate) in vinyl acetate. Ethyl
acetate impurity elutes before the major peak of vinyl acetate.

TABLE II

CAPACITY FACTORS (k') AND RELATIVE RETENTION TIMES $(t_{rel})^a$ FOR SOME UNSATURATED ES-
TERS

Carrier gas, steam; temperature, 108°C; column 200 × 3 mm I.D.

Compounds	Dry salt on solid support											
	$LiNO_3$				$AgNO_3$				$LiNO_3 + AgNO_3$			
	5%		10%		5%		10%		2% + 2%		5% + 5%	
	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}
Ethyl acrylate	0.73	0.73	0.95	0.56	0.5	0.19	0.5	0.17	1.56	0.40	2.10	0.51
Allyl ethyl ether	0.6	0.6	0.79	0.46	0.58	0.22	0.75	0.25	1.72	0.44	2.10	0.51
Allyl methacrylate	0.72	0.72	1à43	0.84	1.08	0.42	1.66	0.55	2.11	0.54	3.36	0.82
Ethyl vinylacetate	1.0	1.0	1.71	1.0	2.58	1.0	3.0	1.0	3.89	1.0	4.08	1.0
Allyl formate	1.55	1.55	2.57	1.50	2.75	1.07	3.17	1.06	4.78	1.23	4.36	1.07

^{a} Internal standard, ethyl vinylacetate.

TABLE III

CAPACITY FACTORS (k') AND RELATIVE RETENTION TIMES (t_{rel})[a] FOR SATURATED AND ALIPHAT-IC ALCOHOLS

Compounds	Dry salt on solid support											
	$LiNO_3$				$AgNO_3$				$LiNO_3 + AgNO_3$			
	5%		10%		5%		10%		2% + 2%		5% + 5%	
	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}	k'	t_{rel}
Methanol	7.5	1.74	13.2	1.51	5.4	1.64	8.33	1.79	8.47	1.72	12.08	1.55
Ethanol	4.3	1.0	8.77	1.0	3.3	1.0	4.66	1.0	4.93	1.0	7.79	1.0
Propanol	3.5	0.81	4.7	0.54	1.8	0.55	3.11	0.67	4.93	1.0	5.2	0.67
Butanol	2.8	0.65	3.6	0.41	1.4	0.42	2.33	0.5	1.33	0.27	4.3	0.55
Amyl alcohol	0.45	0.1	2.23	0.25	0.4	0.12	1.77	0.38	0.93	0.19	0.95	0.12
Allyl alcohol	3.5	0.81	4.42	0.50	59	17.88	262.4	56.31	4.72	0.96	70.7	9.08
Cinnamyl alcohol	16.3	3.79	173.8	19.82	41.4	12.55	146	31.33	13.4	13.4	2.72	-

[a] Internal standard, ethyl vinylacetate.

TABLE IV

RELATIVE RETENTION TIMES FOR SOME ORGANIC COMPOUNDS

Carrier gas, steam–nitrogen mixture; temperature, 80°C.

Compound	Dry salt on solid support			
	5% $LiNO_3$ + 5% $AgNO_3$		10% $LiNO_3$ + 10% $AgNO_3$	
	H_2O pressure[a] (Torr)	H_2O pressure[b] (Torr)	H_2O pressure[a] (Torr)	H_2O pressure[b] (Torr)
Undecane	0.0888	0.0832	0.0921	1.129
Dodecane	0.215	0.207	0.211	0.242
Tridecane	0.471	0.455	0.457	0.492
Tetradecane	1.000	1.000	1.000	1.000
1-Decene	0.371	0.135	0.0679	
trans-2-Decene	0.168	0.079		
cis-2-Decene	0.364	0.193		
trans-3-Decene	0.210	0.073		
cis-3-Decene	0.484	0.146		
trans-4-Decene	0.234	0.066		
cis-4-Decene	0.503	0.123		
trans-5-Decene	0.028	0.058		
cis-5-Decene	0.320	0.093		
Ethanol	0.285	1.0	0.281	0.735
Methanol	0.327	2.029	0.311	1.426

[a] Nitrogen was saturated by passing it through the bubbler at 25°C.
[b] Nitrogen was saturated by passing it through the bubbler at 60°C.

Mixed phases containing $Al(NO_3)_3 \cdot 9H_2O$ or $Zn(NC_3)_2 \cdot 6H_2O$ in addition to silver salts were tested as possible stationary phases for separating both polar and non-polar compounds. Preliminary tests with the use of individual stationary phases for separating *cis* and *trans* isomers of 3-hexene were carried out. Steam–nitrogen was used as the mobile phase. When $Zn(NO_3)_2 \cdot 6H_2O$ was used as the stationary phase, the capacity factors, k', for *cis*-3-hexene and *trans*-3-hexene were 3.67 and 1.33, respectively (temperature 35°C). With $Al(NO_3)_2 \cdot 9H_2O$ as the stationary phase the capacity factors for *cis*- and *trans*-3-hexene were 1.18 and 0.82, respectively (at 78°C).

The separation of unsaturated hydrocarbons on $Al(NO_3)2 \cdot 9H_2O$ was studied with pure steam as the carrier gas at 120°C. A good separation of *cis* and *trans* isomers was achieved. The capacity factors for *cis*-3-hexene, *cis*-2-octene, *trans*-5-decene and *cis*-5-decene were 0.79, 2.72, 4.36 and 5.11, respectively. Both phases were highly selective with respect to *cis* and *trans* isomers of unsaturated compounds. Note, however, that with $LiNO_3$ alone a clear separation of olefinic hydrocarbons was unobtainable when steam–nitrogen was used as the mobile phase. Both *cis* and *trans* isomers and double-bond positional isomers were successfully separated with a mixed $LiNO_3$–$AgNO_3$ stationary phase (Table IV).

When using a sorbent containing 20% $AgNO_3$ on Celite C-22 the best efficiency was found for alkenes [height equivalent to a theoretical plate (HETP) of *cis*-5-tridecene -0.42 mm] and for unsaturated esters (HETP for allyl methacrylate $-$ 0.63 mm). For the alcohols the efficiency was power (HETP for ethanol $=$ 1.2 mm). This can be explained by the especially strong interaction of alcohols with water–salt solutions.

In Fig. 1 the chromatogram of dissolved C_{10}–C_{13} alkenes is shown. Almost all the peaks are symmetrical. The stationary phases investigated are highly selective

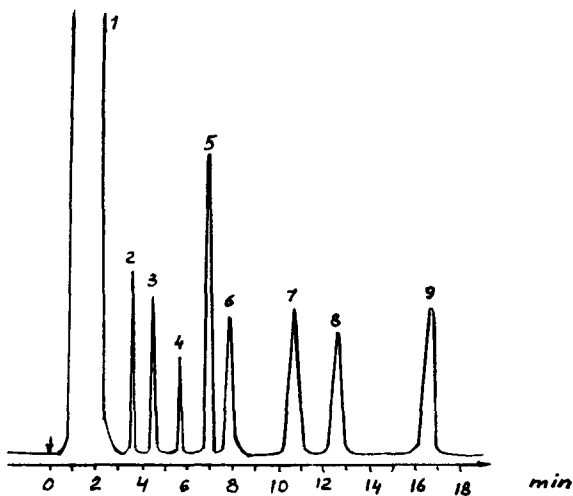Fig. 1. Separation of C_{10}–C_{13} olefins on $AgNO_3$ using steam as the mobile phase at 108°C. Experimental conditions: stationary phase, 20% $AgNO_3$ on Celite C-22; stainless-steel column (2 m × 3 mm I.D.). Peaks: 1 = hexane; 2 = *trans*-5-decene; 3 = 1-decene; 4 = *cis*-5-decene; 5 = *trans*-6-dodecene; 6 = 1-dodecene; 7 = *cis*-6-dodecene; 8 = *trans*-5-tridecene; 9 = *cis*-5-tridecene.

towards alkenes. The difference in the retention indices for decene isomers, $\Delta I = I_{cis\text{-}5\text{-}decene} - I_{trans\text{-}5\text{-}decene}$, is 76 units, *i.e.* the selectivity towards these isomers is essentially higher than that with known polar and non-polar stationary phases. For example, with squalane this difference is 3 units [5], with Apiezon L 2 units [6] and with dibutyl tetrachlorophtalate 6 units [7].

CONCLUSIONS

Pure and mixed inorganic salts impregnated on a solid support with steam as the mobile phase can be used to obtain highly effective packed columns.

The simultaneous use of nitrate solutions (*e.g.*, lithium, aluminium and zinc nitrates) as stationary phase and steam as the mobile phase at 105–110°C permits good separations of *cis* and *trans* isomers of unsaturated hydrocarbons, especially high-boiling C_{13}–C_{14} compounds, to be obtained.

Good separations of polar unsaturated compounds (alcohols and esters) are obtained with steam as the mobile phase and stationary phases containing both pure LiNO$_3$, and a salt mixture (AgNO$_3$ + LiNO$_3$).

The selectivity of the inorganic salt phase deteriorates when the water content in mixed mobile phase decreases, in addition to the temperature of nitrogen saturation with water vapour.

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