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Note

Gas chromatography of organic compounds using inorganic salts as components of the stationary liquid phase and steam as a carrier gas*

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In gas chromatography (GC) the separation of complex mixtures of organic compounds is largely governed by the choice of the selective stationary liquid phase (SLP). Therefore, although the total number of commercially available SLPs used in GC exceeds several hundred[1], the search for new types is continuing.

Previously we have shown the possibility of using a wide range of inorganic salts as components of SLPs stable in the flow of a carrier gas containing steam[2-6]. Of interest is the use of crystal hydrates of inorganic salts, the melting point of which is lower than the temperature at which separation takes place[2,5,6].

When using pure steam as a carrier gas at temperatures above 100°C, not merely the crystal hydrates are in a liquid state but also other salts [6,7].

Poole *et al.*[8] showed that the use of hydrated melts, such as calcium nitrate tetrahydrate, either prevents elution of compounds more polar than halobenzenes at the maximum operating temperature or leads to long retention times and unacceptable peak shape. As the chromatographic process involves the use of an inert gas as the carrier gas, this behaviour is connected with the loss of water by the salt. Phifer and Plummer[9] pointed out the extraordinary selectivity of water as an SLP, which causes the elution order of C_1-C_5 alcohols to be governed by the polarity of the alcohols rather than by their molecular masses. However, they also indicated the instability of water as an SLP. On the other hand, the use of inorganic salts, as adsorbents modified with water vapours does not result in the selectivity usual for water[10].

It is of interest to study the chromatographic characteristics of sorbents containing inorganic salts, *e.g.*, alkali metal salts, capable of stabilizing water in equilibrium with aqueous vapours as a mobile phase at temperatures above 100°C.

EXPERIMENTAL

Use was made of a chromatographic system securing a constant steam content in the mobile phase (Fig. 1) and similar to those used earlier[6]. This system was used in combination with a gas chromatograph LHM-8MD (Khromatograf" works, Moscow, U.S.S.R.), equipped with a flame ionization detector.

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* Dedicated to Dr. E. Heftmann on the occasion of his 70th birthday.

TABLE I

RELATIVE RETENTION VOLUMES OF n-ALCOHOLS (STANDARD, PENTANOL) AND QUANTITY OF WATER ABSORBED (P IS % WATER RELATIVELY TO SALT WEIGHT) FOR THE SORBENT WITH ALKALI METAL SALTS

Temperature = 110°C; pressure at the column entrance is close to the saturated water vapour pressure; the inlet pressure is atmospheric.

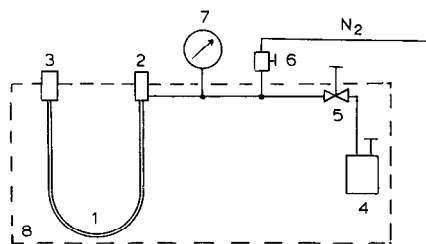| Alcohol	LiCl	NaCl	NaNO$_2$	LiNO$_3$	NaNO$_3$	KCl	KNO$_3$	Na$_2$CO$_3$	Na$_2$SO$_4$	NaHCO$_3$	Na$_3$PO$_4$
Methanol	12.5	7.6	7.5	5.5	4.6	4.45	3.6	0.45	0.15	1.7	0.08
Ethanol	5.7	5.1	3.2	2.9	2.1	2.2	1.8	0.31	0.22	0.8	0.18
Propanol	3.1	3.1	1.7	1.8	1.25	1.25	1.1	0.48	0.45	1.05	0.11
Butanol	1.9	1.7	1.3	1.2	1.0	1.05	1.0	0.65	0.64	1.15	0.48
P_{H_2O} (%)	379	210	210	215	169	130	86	50	6	–	–

Fig. 1. Gas chromatograph for use with water vapour as the mobile phase. 1 = Column; 2 = sample injector; 3 = flame ionization detector; 4 = water vessel; 5 = fine adjustment valve; 6 = stop valve; 7 = pressure gauge; 8 = thermostat.

The solid support was Celite C-22 (60–80 mesh) (Ferak, Berlin) or Inerton N-AW (Lachema, Brno, Czechoslovakia), 0.125–0.16 mm. The sorbent was prepared by deposition of an inorganic salt from its aqueous or ethanol solution in amounts up to 20% (w/w) of the support. The column dimensions were 1–2 m × 2–3 mm I.D. The column temperatures were 110 and 120°C. Water vapour was used as the carrier gas; water consumption rate 3 ml/h. The quantity of water sorbed by the salt was measured by weighing the column after equilibration in the water–steam flow.

RESULTS AND DISCUSSION

A direct relationship was found between the ability of the salt to absorb water and its selectivity (Table I). The ability of salts to retain water and correspondingly to elute alcohols depended on the nature of both the anion and the cation. Thus, the selectivity of sodium salts with respect to alcohols declined in the series NaCl, $NaNO_3$, $NaHCO_3$, Na_2CO_3, Na_2SO_4, Na_3PO_4. Sodium salts had a greater capacity for inversion than potassium salts and a lower capacity than lithium salts. The selectivity decrease is revealed first in a transition from an inversed order of alcohol elution (from pentanol to methanol, columns with LiCl, NaCl, $NaNO_2$, $LiNO_3$, $NaNO_3$, KCl, KNO_3), through partial inversial (on $NaHCO_3$) ethanol first, methanol last, C_3–C_4 alcohols intermediate; on Na_2CO_3, ethanol first, methanol second, followed by C_3–C_4 alcohols to a "normal"order (from methanol to pentanol on columns with Na_2SO_4 and Na_3PO_4). This behaviour is connected with the water content of the sorbents and accordingly with the transition from gas–liquid to adsorption chromatography. Secondly the decrease in selectivity leads to a diminishing distance between the peaks of C_1–C_5 alcohols with decreasing water content in the sorbents. The alcohol peaks were symmetrical for all sorbents during chromatography with steam.

It is interesting that the ability of salts to retain water during the chromatography is not correlated with their ability to form salt crystal hydrates under normal conditions. For example (as is shown in Table I), sodium chloride absorbs much more water than sodium sulphate capable of forming a decahydrate, or sodium phosphate which can form a dodecahydrate. In addition to alkali metal salts, nitrates of other metals, such as aluminium, magnesium and zinc can selectively retain acohols[6].

The dependence of the retention of alcohols on the carbon number is shown in Fig. 2. For sodiumsulphate (curve 1) this reflects the increasing retention in
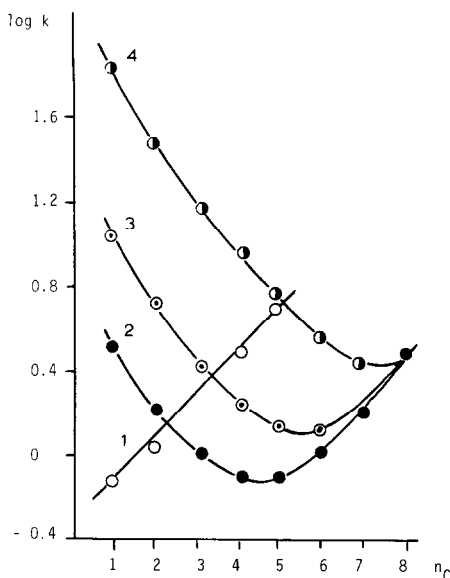
Fig. 2. Logarithmic dependence of the capacity factors (log k) of n-alkanols on carbon number, n_c, for the sorbents with alkali metal salts; 110°C, inlet pressure about 1.4 atm. 1, 20% Na_2SO_4 on Celite C-22; 2, 10% KCl on Inerton N-AW; 3, 20% NaCl on Celite C-22; 4, 20% LiCl on Celite C-22.

homologous series subject to adsorption chromatography. The different behaviour of chloride salt is manifested in curves 2–4. This may be explained by a lower influence of adsorption on the interfaces of the SLP. The left branches of curves 2–4 reflect an increase in solubility with increasing polarity of the compounds chromatographed. This is in accordance with the data of Chatterjee et al.[11] which showed for a water layer on a solid support that with increasing compound polarity the solubility increases but adsorption decreases

As is shown in Fig. 2 for the sorbents containing potassium chloride, sodium chloride and lithium chloride at 110°C, the first compounds eluted are pentanol, hexanol and heptanol respectively. On the column with lithium chloride the C_2–C_9 alcohols are eluted before methanol. So some salts reveal the same or greater selectivity towards polar compounds than does pure water as an SLP.

The ability to retain water and accordingly the selectivity towards alcohols decreases at decreasing water vapour pressure at constant temperature (Table II) and at increasing temperature (Fig. 3).

Fig. 4 shows an example of the analysis of a water layer containing the reaction products of catalytic hydrolysis on a sorbent coated with lithium chloride. This column exhibits the following possibilities. (1) Analysis of pollutants in methanol, since before methanol, compounds both with lower and with higher boiling points are eluted: C_2–C_9 n- and iso-alcohols, ketones, ethers, ester, C_1–C_{17} hydrocarbons. Relative retention volumes are 1.36 for acetone and 0.39 for pentanone-2, 0.29 for ethyl formate and 0.06 for isoamyl acetate (the standard n-pentanol). (2) Analysis of organic pollutants in ethanol, since C_3–C_9 n- and iso-alcohols and other pollutants are eluted before ethanol and what's more the number of them less than at analysis on impurities in
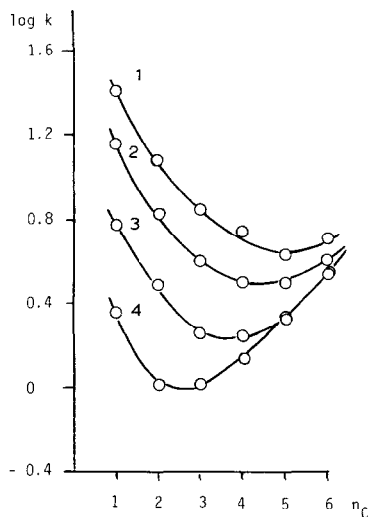
Fig. 3. Logarithmic dependence of the capacity factors of *n*-alkanols (log *k*) on carbon number, n_c, at different temperatures, inlet pressure close to the saturated water vapour pressure. Temperatures: 1, 107°C; 2, 110°C; 3, 114°C: 4, 127°C.
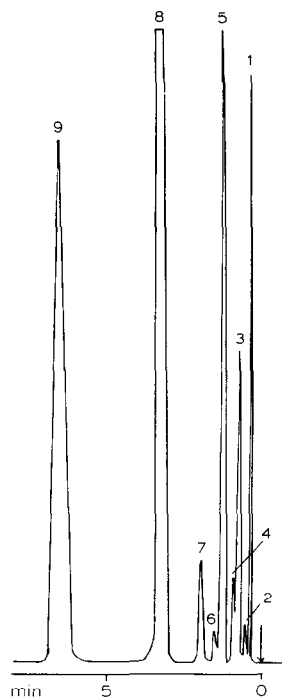
Fig. 4. Chromatogram of polar organic compounds contained in the water layer of hydrolysis reaction products. Column: 190 cm × 2 mm I.D. Sorbent: 7% lithium chloride on Inerton N-AW (0.125–0.16 mm). Temperature: 119°C. Inlet pressure: about 1.9 atm. Carrier gas: water vapour. Peaks: 1 = diethyl ether; 2 = ethyl acetate; 3 = methyl propyl ketone; 4 = methyl ethyl ketone; 5 = acetone and *n*-butanol; 6 = isobutanol; 7 = *n*-propanol; 8 = ethanol; 9 = methanol.

methanol. (3) Selectivity regulation by a small alteration in column temperature; when decreasing the temperature from 119 to 116°C in the analysis of reaction products, the peaks of fourteen rather than nine compounds were revealed. (4) Analysis of aqueous solutions as water is the basis of steam and the SLP. (5) High efficiency: the height

TABLE II

CAPACITY FACTOR, *k*, AND RELATIVE VOLUME, V_{rel}, OF THE LITHIUM CHLORIDE UNDER DIFFERENT INLET PRESSURES, *P*, AT 110°C

10% lithium chloride on Celite C-22 (60–80 mesh)

Solute	k			
	P = 1.125 atm	P = 1.225 atm	P = 1.562	P = 1.70 atm
Methanol	24.57	25.19	28.60	33.27
Pentanol	3.07	3.09	2.78	2.68
V_{rel}	8.00	8.15	10.0	12.40

equivalent to a theoretical plate (HETP) on methanol is near 1 mm. (6) Symmetrical peaks, obviously the inorganic salt solution may decrease the adsorptive activity of the support. (7) Instead of lithium chloride other inexpensive inorganic salts and hydrates of salts can be used at temperatures from 105 to 150°C. Not only alkali metal salts but also other salts are useful. For example, the retention volumes of methanol relative to pentanol are: 7.4 for $Cu(NO_3)_2$, 7.2 for $Cd(NO_3)_2$, 3.5 for $Zn(NO_3)_2$, 2.25 for $CuSO_4$ and 1.65 for $CoCl_2$.

Sufficiently high efficiency can be obtained and under a high mobile phase flow-rate. So with increasing oven temperature up to 127°C, the mobile phase flow-rate through the packed column increased to 20 cm/s, *i.e.*, about five times as that deemed, as a rule, to be optimal for a packed column (3–4 cm/s). In this case, for the column of 2 mm I.D. with sodium chloride the HETP increases only to 2 mm for methanol, propanol and pentanol. This can be associated with a low molecular mass transfer rate.

Thus, for a selective GC separation of polar and non-polar organic compounds it appears practicable to use the system water–inorganic salts as an SLP with steam as a mobile phase. The use of inexpensive and accessible inorganic salts allows selective and stable resolution of complex organic mixtures which can be obtained as a rule only by use of high efficiency capillary columns.

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