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## EUTECTIC INORGANIC SALT MELTS AS STATIONARY PHASES FOR GAS CHROMATOGRAPHIC SEPARATION OF HIGH-BOILING HYDROCARBONS

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### SUMMARY

The thermal stability of nine eutectic inorganic salts with melting temperatures between 80 and 180°C was evaluated. The contact angles of six of these salt melts on glass and PTFE are similar to that of 1,2,3-tris-(2-cyanoethoxy)propane, a strongly polar organic phase. Packed and capillary columns with salt melts as stationary phase were prepared. It appears that the retention mechanism of hydrocarbons on salt melts is dominated by adsorption at the liquid surface. The separation is strongly dependent on the sample size. Packed columns with 700 and capillary columns with up to 2000 theoretical plates per metre could be prepared. An example is given of the separation of a *n*-alkane mixture with an average molecular weight of 628.

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### INTRODUCTION

A great number of different solid inorganic salts have been used as stationary phases in gas-solid chromatography and as polarity modifiers for organic phases in gas-liquid chromatography<sup>1,2</sup>. In comparison, the use of salt melts as separation phases has been little studied. The separation of volatile transition metal halides by means of salt melts has been reported<sup>3</sup>. Polyphenyls, crude oils, cyclic hydrocarbons and alkanes up to *n*-C<sub>40</sub> have been separated by use of mixtures of potassium, lithium and sodium nitrates and lithium and caesium chlorides above their respective melting points in packed columns<sup>4-6</sup>. Until now, no reports on the use of molten salts in capillary gas chromatography (GC) have been made.

Organic salt melts show only a limited temperature stability<sup>7</sup>. Their retention behaviour is similar that of other organic stationary phases. Certain inorganic salt melts are stable at high temperatures. Compared to organic stationary phases, they should show advantages when high-boiling compounds are to be separated. In addition, their separation efficiency should be higher than that of solid phases which is limited by surface heterogeneity.

In the present communication new findings on the stability of low-melting inorganic salt melts, the preparation of packed and capillary columns of salt melts,

their separation mechanism and efficiency and the separation of *n*-alkanes up to *n*-C<sub>55</sub> are reported.

## EXPERIMENTAL

The eutectic salt melts with their respective compositions and melting temperatures are listed in Table I. All salts were of analytical grade.

Chromosorb W AW, G-DMCS, etched glass beads TGB, normal 80-mesh glass beads and Fluoropack F80 were used as solid supports. The water-soluble salts were dissolved in water after which the support was added. The resulting slurry was dried by rotary evaporation. Wettability of the support was improved by adding a small quantity of Tenside FC 126 (3M Co., St. Paul, MN, U.S.A.) which evaporates completely after heating at 180°C. AgI-AgNO<sub>3</sub>, CuCl-KCl and CuBr-KBr were applied as triethylamine and hydrochloric acid solutions, respectively.

Glass capillaries were drawn from AR and Duran 50 glass, and etched by NH<sub>4</sub>HF<sub>2</sub><sup>8</sup>. After etching, careful rinsing with an aqueous methanol solution removed the remaining salts. The capillary column was dynamically coated with aqueous solutions of the eutectic salts. The KNO<sub>3</sub>-LiNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> eutectic was applied as a 8% coating solution. A too high viscosity of the coating solution is to be avoided. The column was dried in a nitrogen stream at 150°C. Heating at 1°C/min up to 350°C was followed by a 24-h conditioning period.

A Varian GC-3700 gas chromatograph equipped with an all-glass splitter and a flame ionization detector was employed. The output signal of the electrometer amplifier of the detector was fed to a 16-bit analog-to-digital converter coupled with a CBM 3016 (Commodore) micro-computer. In this way, the variance and consequently the theoretical plate numbers could be determined from asymmetric peaks according to the procedure suggested by Sternberg<sup>9</sup>.

The contact angles of the melts on PTFE and glass were measured with the Erna G1 (Erna, Tokyo, Japan). The cleaned glass and PTFE surfaces were heated to a temperature above the melting point of the eutectic salt, the salt was applied and

TABLE I  
PROPERTIES OF EUTECTIC SALT MELTS INVESTIGATED

<i>Eutectic</i>	<i>Composition (mass-%)</i>	<i>Melting temp.* (°C)</i>	<i>Stability temp.** (°C)</i>
KNO <sub>3</sub> -Ca(NO <sub>3</sub> ) <sub>2</sub> -Mg(NO <sub>3</sub> ) <sub>2</sub>	53:41:6	137	450
KNO <sub>3</sub> -LiNO <sub>3</sub> -Ca(NO <sub>3</sub> ) <sub>2</sub>	62:23:15	117	420
Cd(NO <sub>3</sub> ) <sub>2</sub> -NaNO <sub>3</sub> -LiNO <sub>3</sub>	56:30:14	110	400
Cd(NO <sub>3</sub> ) <sub>2</sub> -KNO <sub>3</sub> -LiNO <sub>3</sub>	76:18:6	111	400
TiNO <sub>3</sub> -AgNO <sub>3</sub> -KNO <sub>3</sub>	54.8:44:1.2	79	420
AgI-AgNO <sub>3</sub>	53.5:46.5	105	260
KNO <sub>3</sub> -LiNO <sub>3</sub>	66:34	129	450
CuCl-KCl	73:27	136	200
CuBr-KBr	67:33	182	200

\* Data from ref. 11.

\*\* Maximum temperature for mass changes ≤ 0.1%/day.

as soon as the melt droplet had stabilized the system was quenched to room temperature and the contact angle measured.

The stability of the salt melts in a nitrogen stream was measured on a Stanton TR-1 thermogravimetric balance. A Perkin-Elmer DSC-1 differential scanning calorimeter was used to determine the melting characteristics of the salts on the support phases.

## RESULTS AND DISCUSSION

The melting and stability temperatures of the eutectic salts investigated are listed in Table I. The stability temperature is the temperature below which the salt melt shows mass changes of  $\leq 0.1\%$  after heating for 24 h in a nitrogen stream. Most stable low-melting eutectic salts contain alkali-metal nitrates. Generally, at the stability temperature a mass loss caused by evaporation or decomposition is observed. However, copper(I) salts are easily oxidized by traces of oxygen in the nitrogen stream, and show a mass increase at their stability temperature.

The coating efficiency depends on the viscosity and on the spreading behaviour of the liquid stationary phase. The viscosity of the alkali-metal nitrates at  $300^\circ\text{C}$  is well below 4 cP and should cause no particular problems. The contact angles of eutectic salt melts and common organic stationary phases on glass and PTFE are compared in Table II. The spreading behaviour of inorganic salt melts and 1,2,3-tris(2-cyanoethoxy)propane (TCEP), a strongly polar organic phase, is similar.

DSC thermograms were used to compare the phase transitions of the salts on the solid support with their bulk melting points.  $\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2$  and  $\text{AgI-AgNO}_3$  on solid support phases showed broad phase transition ranges from  $90$  to  $140^\circ\text{C}$  and  $89$  to  $116^\circ\text{C}$ , respectively. The melting range of the other eutectic salts investigated was less than  $10^\circ\text{C}$ .

The polar Chromosorb W AW was recommended as a support for salt melts<sup>6</sup>. Packed columns of pure Chromosorb W AW and Chromosorb W AW coated with 5 and 30 mass-% of the  $\text{KNO}_3\text{-LiNO}_3$  eutectic were prepared. On these columns the net retention times of saturated and aromatic hydrocarbons, at temperatures above the melting point of the salt phase, showed only small differences.

TABLE II

CONTACT ANGLES OF ORGANIC PHASES AND INORGANIC EUTECTIC SALT MELTS ON GLASS AND PTFE

Phase	Contact angle (degree)	
	AR glass	PTFE
Squalane	13	45
Carbowax 20M	11	75
TCEP	62	87
$\text{Cd}(\text{NO}_3)_2\text{-KNO}_3\text{-LiNO}_3$	45	93
$\text{Cd}(\text{NO}_3)_2\text{-NaNO}_3\text{-LiNO}_3$	59	75
$\text{KNO}_3\text{-LiNO}_3\text{-Ca}(\text{NO}_3)_2$	90	100
$\text{KNO}_3\text{-Ca}(\text{NO}_3)_2\text{-Mg}(\text{NO}_3)_2$	75	105
$\text{TlNO}_3\text{-AgNO}_3\text{-KNO}_3$	76	96
$\text{KNO}_3\text{-LiNO}_3$	74	99

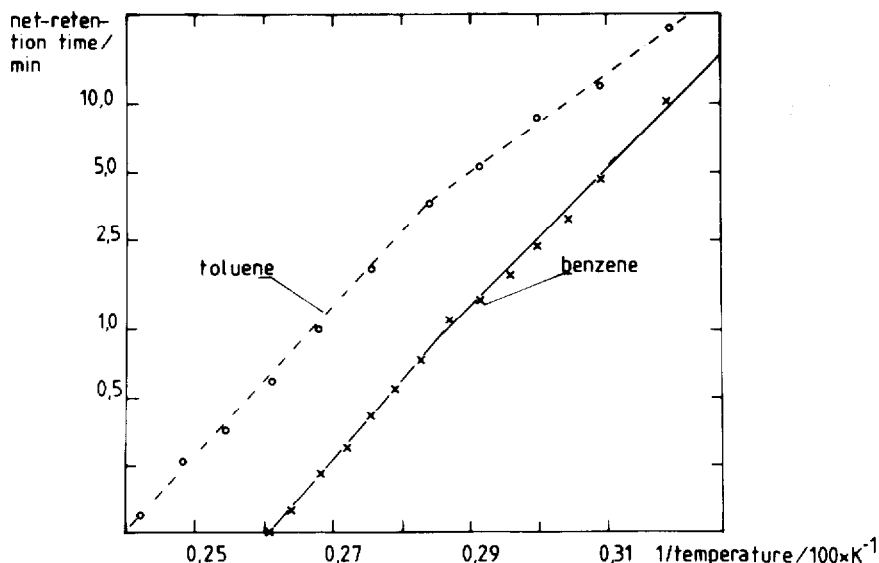


Fig. 1. Net retention times of benzene (×) and toluene (○) as a function of the column temperature on a 1 m × 1/8 in. I.D. stainless-steel column packed with 30 mass-%  $\text{TiNO}_3\text{-AgNO}_3\text{-KNO}_3$  eutectic melt on glass beads. Carrier gas (nitrogen) flow-rate: 20 ml/min.

It seems that the salt melt does not cover the support surface completely even at loadings of 30 mass-%. Adsorption on the support surface dominates the retention mechanism. Addition of the salt melt reduces only peak asymmetry. These findings suggest that most previously reported separations on inorganic salt melt columns were in fact controlled to a large extent by gas-support adsorption. Consequently, in order to study retention on salt melts, an apolar support like Chromosorb G-DMCS, glass or PTFE beads should be used.

Fig. 1 shows the temperature dependence of the net retention times of benzene and toluene on a  $\text{TiNO}_3\text{-AgNO}_3\text{-KNO}_3$  eutectic phase. In each case the data can be represented by two straight lines which meet at 80°C and 82°C, respectively. This is the melting range of the salt phase. Melting of the stationary phase obviously has little effect on the retention mechanism. The retention times are insensitive towards a change of the stationary phase loading. The asymmetry of the elution peaks increases with sample size. A sample as small as is compatible with the general noise level should be injected in order to obtain symmetrical peak shapes. Considering all these observations, it appears that adsorption dominates the retention mechanism of hydrocarbons on inorganic salt columns: below the melting point, adsorption at the solid-salt surface; above the melting point, adsorption at the surface of the salt melt.

McReynolds constants could not be determined for the inorganic salt melts because of insufficient retention of the standard probes.

The number of theoretical plates of a column packed with 30 mass-% of a  $\text{KNO}_3\text{-LiNO}_3\text{-Ca(NO}_3)_2$  eutectic on Chromosorb G-DMCS between 150 and 190°C was determined using *n*-pentadecane and *n*-octadecane. The maximum plate count observed was 740 theoretical plates per metre. The minimum in the van Deemter plot occurred at a carrier gas (nitrogen) velocity of 10 ml/min. Capillary columns with an

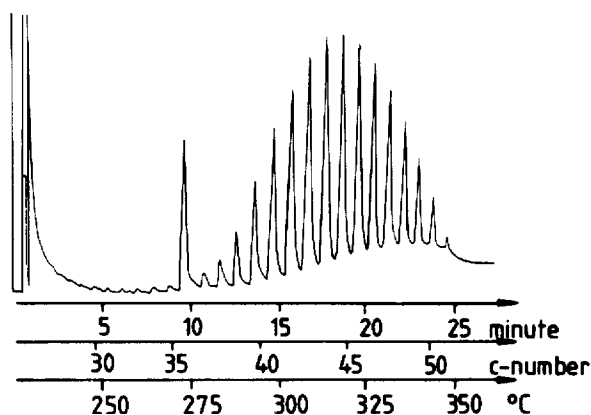


Fig. 2. Separation of a *n*-alkane mixture on a 3 m × 1/8 in. I.D. stainless-steel column packed with 30 mass-%  $\text{KNO}_3$ - $\text{LiNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  eutectic melt on Chromosorb G-DMCS. Heating rate: 5°C/min from 230°C to 400°C.

inner diameter of 0.3 mm were also coated with the  $\text{KNO}_3$ - $\text{LiNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  eutectic. The plate number was found to decrease with sample size. However, up to 2000 theoretical plates per metre could be achieved.

Fig. 2 shows the temperature-programmed separation of a *n*-alkane mixture on a  $\text{KNO}_3$ - $\text{LiNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  eutectic. The molten salt phase separates the *n*- $\text{C}_{30}$ -*n*- $\text{C}_{55}$  alkanes. *n*-Pentacontane is eluted at 340°C after 24 min. The average molecular weight, 628, of this sample, as determined from the gas chromatogram, is within 2% of the value determined by vapour osmometry.

Separation at temperatures as high as 350°C is only possible for substances that show the necessary thermal stability. Decomposition reactions may be catalysed by the salt melt<sup>10</sup>. Fortunately, retention on salt melts is generally low. For example, Fig. 2 shows the elution temperature for the  $\text{KNO}_3$ - $\text{LiNO}_3$ - $\text{Ca}(\text{NO}_3)_2$  melt to be 50°C lower than that for a comparable Dexsil 300-coated column.

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#### REFERENCES

- 1 V. Schurig, *Chromatographia*, 13 (1980) 263.
- 2 H. Trautler and M. Rossier, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 189.
- 3 R. S. Juvet and F. M. Wachi, *Anal. Chem.*, 32 (1960) 290.
- 4 W. W. Hanneman, C. F. Spencer and J. F. Johnson, *Anal. Chem.*, 32 (1960) 1386.
- 5 P. W. Solomon, *Polyphenol Analysis*, Atomic Energy Commission research and development report, TID-4500, 1964.
- 6 L. R. Snowden and E. Peake, *Anal. Chem.*, 50 (1978) 379.
- 7 F. Pacholec and C. F. Poole, *Chromatographia*, 17 (1983) 370.
- 8 F. Onuska and M. Comba, in R. E. Kaiser (Editor), *2nd International Symposium on Glass Capillary Chromatography, Hindelang 1977*, Institut für Chromatographie, Bad Dürkheim, 1977, p. 283.
- 9 J. C. Sternberg, in *Advan. Chromatogr.*, 2 (1966) 205.
- 10 W. Sundermeyer, *Angew. Chem.*, 77 (1965) 241.
- 11 G. J. Janz, *Molten Salts Handbook*, Academic Press, New York, 1967.