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## SEPARATION OF AROMATIC AND SULPHUR-CONTAINING HYDROCARBONS ON PURE AND DISPERSED CHLORIDES AND SULPHATES OF A SERIES OF BIVALENT METALS

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### SUMMARY

Inorganic salts have been used for the high-speed gas chromatographic separation of mixtures of aromatic compounds and sulphur-containing hydrocarbons. The adsorbents used were prepared on the basis of structurally different chlorides of bivalent metals ( $\text{NiCl}_2$ ,  $\text{CoCl}_2$  and  $\text{BaCl}_2$ ). An independent method has been developed in order to evaluate the uniformity of the salt crystals. The salts were studied in the pure form and also dispersed on the surface of Silochrom.

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### INTRODUCTION

Recently, inorganic salts have been used successfully for the gas chromatographic separation of complex mixtures of components that do not differ greatly in their physico-chemical properties (for reviews, see refs. 1-3). The advantages of salts as adsorbents in gas chromatography are their high thermal stability and the possibility of changing the specific adsorption properties of their surfaces. In a previous paper<sup>1</sup>, we showed that barium sulphate possesses high specificity in relation to unsaturated and aromatic hydrocarbons (at relatively low total adsorption energies) and effectively separates isomeric unsaturated and alkyl-aromatic hydrocarbons (especially the xylenes), polyphenyls and polynuclear aromatic hydrocarbons.

This paper describes the adsorption properties and gas chromatographic applications of the chlorides of bivalent metals with different crystal structures, *viz.*  $\text{NiCl}_2$  and  $\text{CoCl}_2$ , which have layered crystal structures, and also  $\text{BaCl}_2$ , which has a non-layered crystal structure.

### EXPERIMENTAL

#### *Materials*

The specific surface areas,  $s$ , were determined by low-temperature adsorption of nitrogen using either the B.E.T. or thermal desorption method, and were found to be  $1.0 \text{ m}^2/\text{g}$  for  $\text{BaCl}_2$ ,  $12 \text{ m}^2/\text{g}$  for  $\text{NiCl}_2$  and  $6.0 \text{ m}^2/\text{g}$  for  $\text{CoCl}_2$ . Studies were also made

on samples obtained by precipitating the salts from aqueous solutions on to the surface of Silochrom, for which  $s = 80 \text{ m}^2/\text{g}$ , the amounts of the salt precipitated being 5, 10, 20 and 25% (w/w) of the Silochrom. For these modified Silochroms,  $s$  was in the range 40–70  $\text{m}^2/\text{g}$  (ref. 3).

### *Apparatus*

The adsorption measurements were carried out by the volumetric method on a vacuum adsorption apparatus using electromagnetic stopcocks made from glass-PTFE. The gas chromatographic measurements were performed using a Tswett-3 chromatograph with flame ionization detector. The glass columns had the dimensions  $1 \text{ m} \times 3 \text{ mm}$  I.D. and  $2 \text{ m} \times 4.5 \text{ mm}$  I.D. The flow-rate of the carrier gas (nitrogen) was 48–55 ml/min and the measurements were carried out at temperatures from 120 to 250 °C. The salts, either in the pure state or precipitated on Silochrom, were evacuated to a pressure of  $5 \times 10^{-2}$  mm Hg before the measurements by slowly heating  $\text{BaCl}_2$  to 200 °C,  $\text{NiCl}_2$  to 250 °C and  $\text{CoCl}_2$  to 275 °C. During the gas chromatographic studies, the sample was subjected to supplementary heating in the column in the stream of carrier gas.

## RESULTS AND DISCUSSION

For gas chromatographic studies, the uniformity of the surface of the adsorbent is of primary importance and it was therefore necessary to develop an independent method for the evaluation of the uniformity of the surface. The identification and determination of the surface area of the uniform parts of the surfaces of crystalline adsorbents is suggested for this purpose, based on the application of the phase transformation of xenon at temperatures lower than the critical temperature of the two-dimensional state. As an example, Fig. 1 shows the adsorption isotherms of xenon at 78 °K on some of the supports studied. The adsorption isotherms of xenon on a sample of  $\text{CoCl}_2$  evacuated at 110 °C have seven vertical steps<sup>3</sup> and, as the temperature of evacuation is increased, the number of vertical steps is decreased. The adsorption isotherms of xenon on  $\text{CoCl}_2$  evacuated at 325 °C show two vertical steps up to the point when the whole surface is covered with a monolayer (Fig. 1a). As the appearance of vertical steps on the isotherms at low temperature may be due to two-dimensional condensation of the adsorbate on the uniform part of the surface, it follows that the total surface of these samples consists of two types of physically uniform parts. Hence the existence of two vertical steps is related to the two-dimensional condensation of xenon on different faces, one of which seems to be the base crystal face (0001), which contains only chlorine ions, and the other face is (10 $\bar{1}$ 4), which contains chlorine and metal ions.

For those samples which were obtained by dispersing the chlorides on Silochrom, the xenon isotherms show one vertical step (Fig. 1b), which indicates that the modified chloride adsorbents are sufficiently uniform.

The specificity of the samples for aromatic hydrocarbons was evaluated gas chromatographically by measuring the retention volumes and the initial heats of adsorption of the corresponding compounds. For  $\text{NiCl}_2$  and  $\text{CoCl}_2$ , which have a layer structure with the  $\text{Cl}^-$  ions on the base face (0001) and the  $\text{Cl}^-$  and  $\text{M}^{2+}$  ions ( $\text{M} = \text{metal}$ ) on the (10 $\bar{1}$ 4) face, the contribution of the energy of specific interaction

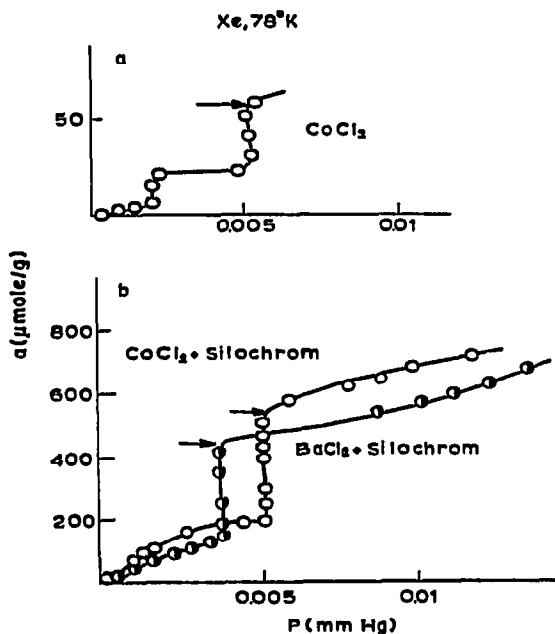


Fig. 1. Adsorption isotherms of xenon at 78 °K on CoCl<sub>2</sub> evacuated at 325 °C for 16 h ( $s = 6 \text{ m}^2/\text{g}$ ) and on samples of 10% CoCl<sub>2</sub> + Silochrom evacuated at 270 °C for 20 h ( $s = 58 \text{ m}^2/\text{g}$ ) and 10% BaCl<sub>2</sub> + Silochrom evacuated at 200 °C for 24 h ( $s = 52 \text{ m}^2/\text{g}$ ). The arrows indicate the capacity values of the compact monolayers of xenon on the whole surface.

of aromatic hydrocarbons to the total adsorption energy is 2.2 kcal/mole. This value is lower than that for BaCl<sub>2</sub> (6.5 kcal/mole), in which all faces of its surface contain both Cl<sup>-</sup> and Ba<sup>2+</sup> ions. The retention volumes of aromatic hydrocarbons per unit surface area of BaCl<sub>2</sub> are much greater (by 30 times) than those for CoCl<sub>2</sub> and NiCl<sub>2</sub> (Fig. 2). When the chlorides are heated to 250 °C, the values of the retention volumes of hydrocarbons are virtually unchanged (Fig. 2).

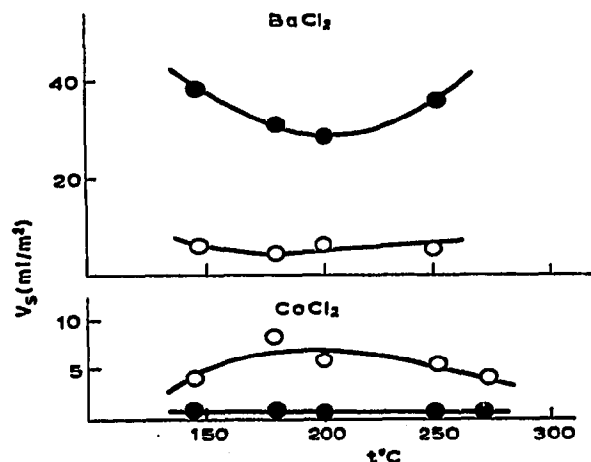


Fig. 2. Retention volumes of benzene (●) and *n*-nonane (○) per unit surface area at 140 °C for BaCl<sub>2</sub> and CoCl<sub>2</sub> versus their temperature of pre-heating in the chromatographic column.

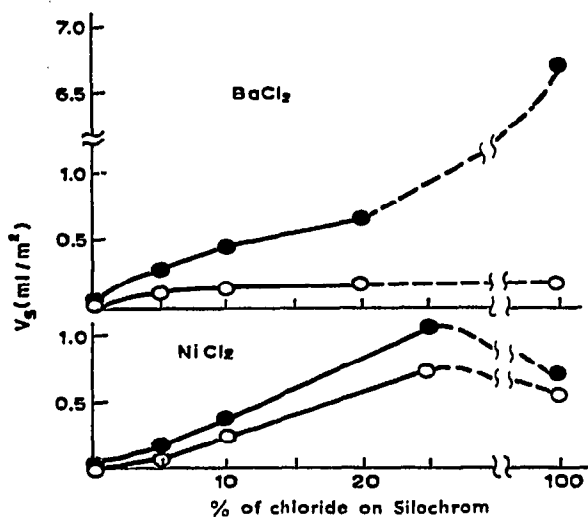


Fig. 3. Retention volumes of toluene (●) and *n*-octane (○) per unit surface area versus the amount of the salts dispersed on Silochrom for BaCl<sub>2</sub> at 180 °C and NiCl<sub>2</sub> at 200 °C; 100% represents the pure salts.

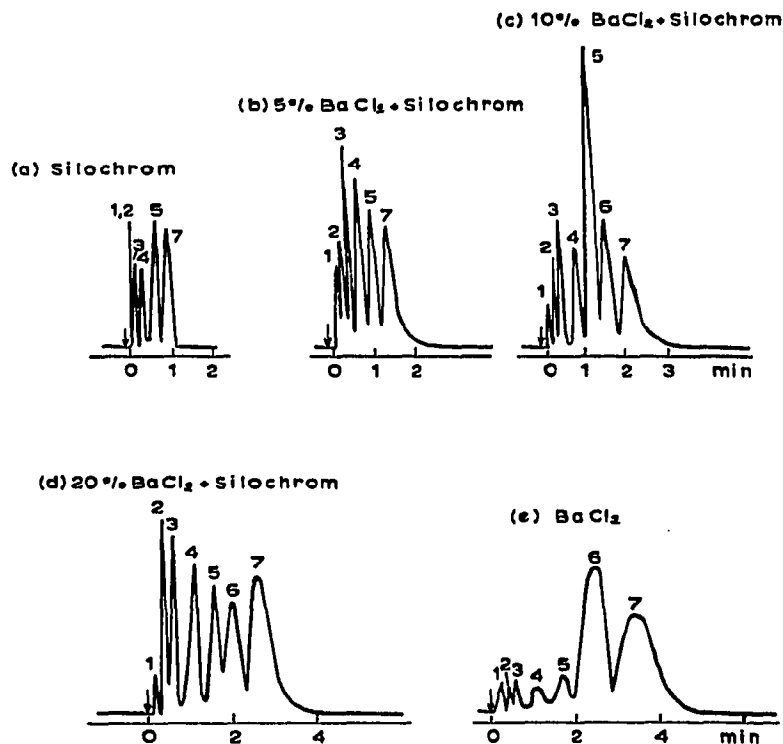


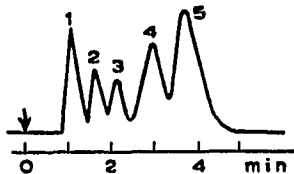
Fig. 4. Chromatograms of a mixture of aromatic hydrocarbons on (a) Silochrom, (b), (c), (d) Silochroms modified with different amounts of BaCl<sub>2</sub> and (e) pure BaCl<sub>2</sub>. Column temperature, 200 °C; length, 1 m; I.D., 4.5 mm; carrier gas flow-rate, 50 ml/min; flame ionization detector. 1 = Cyclohexane; 2 = cyclohexane; 3 = benzene; 4 = toluene; 5 = ethylbenzene; 6 = isopropylbenzene; 7 = *p*-xylene.

When the Silochrom is modified by the chlorides of nickel, cobalt and barium, there occurs a chemical interaction between the hydroxyl groups of the Silochrom and the chlorides. As with pure salts, the modified samples have larger retention volumes for aromatic hydrocarbons than for normal hydrocarbons. The retention volumes of hydrocarbons per unit surface area for the modified samples increase with increasing amount of chloride dispersed (Fig. 3).

Compounds that contain double bonds, aromatic hydrocarbons and bromothiophenes are well separated on both the pure salts and on Silochrom modified by those salts. All of the salts studied so far permit the rapid and complete separation of mixtures of practical interest containing alkylbenzenes and xylenes. The analysis of mixtures containing ethylbenzene and xylene at 200 °C on samples prepared on the basis of  $\text{BaCl}_2$  is achieved in 1.5–2.5 min, *i.e.* these samples can be used in high-speed chromatographic analysis (Fig. 4).

Fig. 4 shows also that when the chlorides are dispersed on Silochrom, a more effective adsorbent is obtained compared with the pure chlorides. In addition, when the amount of  $\text{BaCl}_2$  dispersed on Silochrom is increased, the selectivity of the adsorbent for aromatic hydrocarbons is increased. However, in spite of this high specificity, on  $\text{BaCl}_2$  the xylenes are not separated. These isomers are separated on salts that contain complex anions, such as  $\text{BaSO}_4$ , for which the contribution of the energy of specific interaction in relation to benzene is 5.5 kcal/mole for a total heat of adsorption of 12 kcal/mole (refs. 1 and 3).

(a)  $\text{BaCl}_2$  + Silochrom



(b)  $\text{CoCl}_2$  + Silochrom

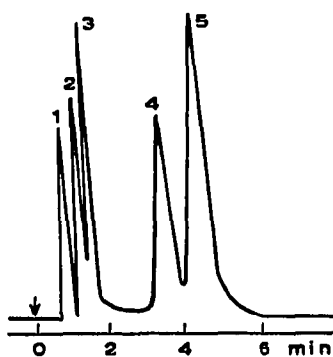


Fig. 5. Chromatograms of a mixture of mono- and dibromothiophenes on (a) 10%  $\text{BaCl}_2$  + Silochrom and (b) 10%  $\text{CoCl}_2$  + Silochrom. Column temperature, (a) 180 °C and (b) 160 °C; length, 2 m; I.D., 3 mm; carrier gas flow-rate, 50 ml/min; flame ionization detector. 1 = Thiophene; 2 = 2-bromothiophene; 3 = 3-bromothiophene; 4 = 2,3-dibromothiophene; 5 = 3,4-dibromothiophene.

Biologically active isomers of bromo- and dibromothiophenes have been separated on the chlorides studied. When pure Silochrom is used, these isomers are very strongly retained and are not eluted from the column. On pure  $\text{NiCl}_2$  and  $\text{CoCl}_2$ , the isomers are eluted rapidly but are not separated, but when these salts are spread on Silochrom they are effectively separated (Fig. 5)<sup>3</sup>.

These studies carried out with salts and with Silochrom modified by the same salts thus permit the formation of uniform surfaces with different specificities of intermolecular interaction, the selectivity and the effectiveness of which can be regulated in relation to aromatic hydrocarbons and their derivatives.

#### ACKNOWLEDGEMENT

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