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POLYMERIC SCHIFF BASE COMPLEXES AS SOLID PHASES IN GAS CHROMATOGRAPHY

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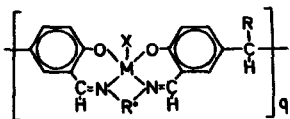
SUMMARY

The efficiency of polymeric Schiff base complexes as solid phases for the chromatographic separation of low-molecular-weight gases was tested with respect to three variations of the complexes: the central metal ion, the amine bridge and substitution of the methylene group between the two aromatic rings. An optimum effect was achieved with V^{2+} and Cr^{2+} as central ions, a C_4 - C_6 chain between the two nitrogen atoms and either one toluene or cumene group on the methylene bridge. Some special effects concerning the separation of O_2 are mentioned.

INTRODUCTION

A large number of polymeric Schiff base complexes with a variety of central metal ions and ligand systems was synthesized recently^{1,2}. Most of these complexes exhibit an unusual adsorptive behaviour with different solvents, very similar to those of molecular sieves³⁻⁵. The use of such complexes as a solid phase in gas chromatography (GC) was discussed in preliminary reports^{3,6}. In this paper a more detailed description of this application is given and attempts to optimize the separation efficiency with respect to the central metal ion and certain variations of the ligand system are reported.

With liquids, mainly benzene and its 1,3,5-alkene-substituted derivatives, it was shown that the adsorption capacity of the polymeric Schiff base complexes depends on the central ion M^{n+} , the hydrocarbon bridge, R' , between the nitrogen atoms and the substituent R on the methylene group linking the aromatic rings^{4,5}.



However, as a solid phase for GC separations, only one complex ($M = Cr^{2+}$, $R' = C_6H_{10}-CH_2-C_6H_{10}$, $R = H$) has been tested so far^{3,6}.

EXPERIMENTAL

All complexes were synthesized according to methods described previously^{1,2}. They were dried first in vacuum at 95°C for several hours and then at 150°C. A grain size of 0.2–0.4 mm was selected by sieving. The GC columns (1800 mm, four windings, 3 mm I.D.) were filled by suction of the complex into the injector end using a vacuum at the detector end. Pressure should not be applied since it changes the surface in such a way that the adsorption capacity of the complexes is strongly reduced⁷.

The filled columns were again heated first at 175°C for 1 h, then at 225°C for 1 h, maintaining a high flow-rate of carrier gas (50–100 ml/min). Since solvent molecules are still desorbed under these conditions, there may be a shrinkage in the complex volume of up to 30%, which necessitates supplementary refilling of the column under identical conditions. The complexes were finally activated by heating to 250°C overnight with 30 ml/min of carrier gas.

All measurements were carried out with a Carlo Erba Strumentazione Fractovap 4200 with HWD-Control 405 and FID Electrometer 180. Gas chromatograms were plotted with a Spectra-Physics SP 4100.

Fig. 1 shows a separation of the noble gases obtained with one of the most efficient complexes. As the dead time is not exactly known, but the retention time of He/Ne is always very short and shows little variation (0.30–0.56 min) on all the complexes, we used it as a pseudo-dead time and the efficiencies presented in Figs. 2–4 are given in terms of the relative retention time of Xe: $R'_i(\text{Xe}) = R_i(\text{Xe}) - R_i(\text{He/Ne})$. All other conditions of these measurements are as in Fig. 1.

For the separation of higher-molecular-weight gases or those of greater polarity, the temperature has to be raised. The upper limit for this is set by the decomposition temperature of the complexes, which is between 250 and 300°C^{1,2}. Thus, non-polar hydrocarbons having up to six carbon atoms may be separated, but less than six when the compounds are polar, using the complexes discussed in this paper (see Fig. 9). This limit may be somewhat extended by using complexes with a lower adsorption capacity like that of the beryllium complex.

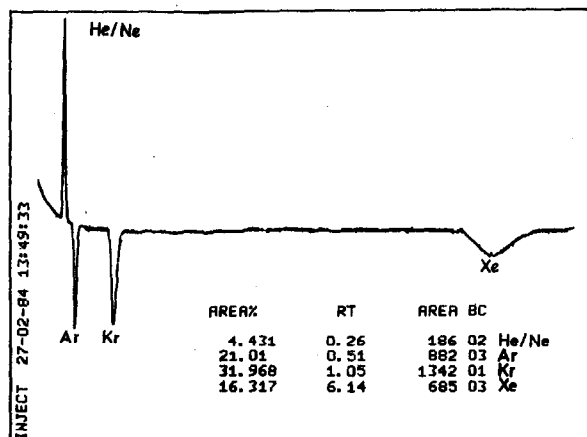


Fig. 1. Separation of noble gases (30 ml N₂/min, 20°C). Complex: R = *p*-tolyl, R' = (CH₂)₆, M = Cr²⁺.

RESULTS

Dependence of column efficiency on the metal ion

Fig. 2 shows the relative retention times, $R'_t(\text{Xe})$, on the complexes with divalent cations of the first-row transition elements (V^{2+} to Zn^{2+}) with two different amine bridges and for the trivalent ions of these elements (Ti^{3+} to Co^{3+}) with the diaminobutane bridge. There is a steady decrease of column efficiency along the series of divalent ions; V^{2+} and Cr^{2+} give the best, then come Mn^{2+} and Fe^{2+} with considerably lower values and there is another sharp decrease to Co^{2+} with only a small variation on going to Zn^{2+} . Apparently the higher the column efficiency the lower is the number of d electrons present, although for completely empty or filled d orbitals, as is the case with group IIB main-group elements, the efficiency is lowest. Of the main-group elements, only beryllium complexes are able to separate the noble gases. On going to higher oxidation states, which implies additional ligands on the metal ion besides the organic Schiff base, the column efficiency is reduced. Thus, complexes with trivalent metal ions are always poorer molecular sieves than those with corresponding divalent ions. However, a steady trend along the transition series is not observable for the trivalent ions. For tetravalent central ions no separation is observed at all.

Dependence of column efficiency on substituents at the methylene bridge

In a previous paper⁵ it was shown, that substitution by phenyl derivatives of one hydrogen atom at the bridging methylene group considerably enhances the adsorption capacity. In Fig. 3 it is seen that this is also the case for the efficiency of these complexes as the solid phase in gas chromatography. *p*-Alkyl substitution increases the retention time of Xe even more, but for a biphenyl group the retention falls to values between those of the phenyl derivative and of the unsubstituted compound. *p*-Cumene derivatives have the highest efficiencies, followed by the *p*-toluene compounds.

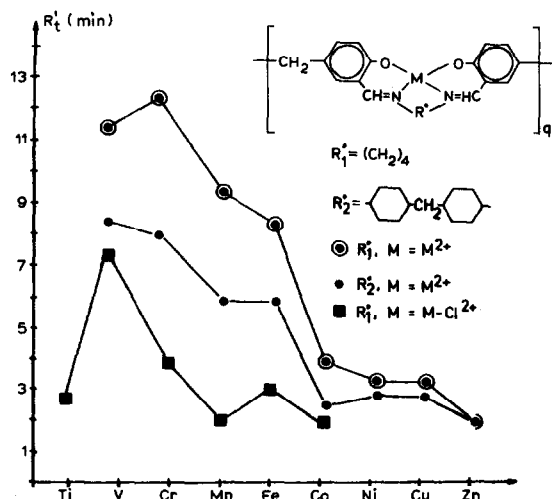


Fig. 2. Dependence of the column efficiency on the central metal ion.

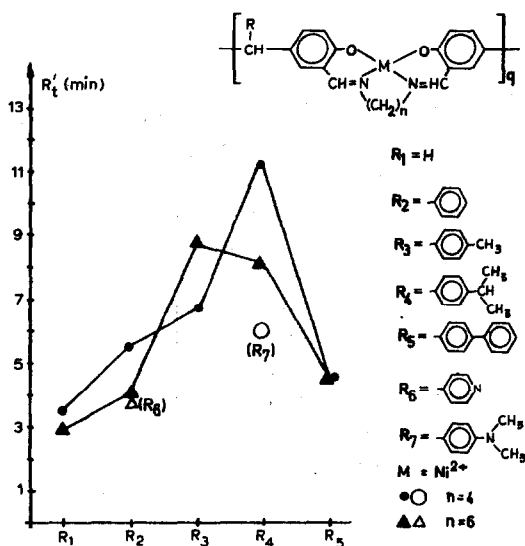


Fig. 3. Dependence of the column efficiency on the substituents at the methylene bridge.

We have also tested the influence of more polar substituents. From Fig. 2 it is seen that the effect of substituting a 4-pyridyl for a phenyl group and a 4-dimethylaniline for a 4-cumyl group is to reduce the retention time of Xe.

Dependence of column efficiency on the length of the amine bridge

Fig. 4 shows the dependence of the relative retention time of Xe on the amine

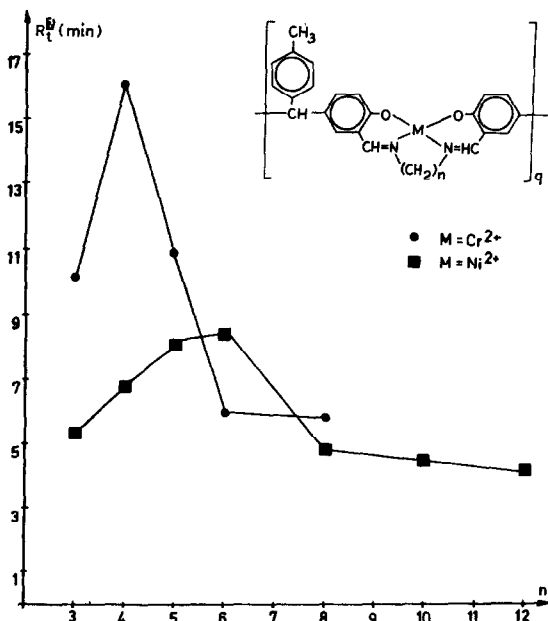


Fig. 4. Dependence of the column efficiency on the length of the diamine bridge.

bridge, which consists of an unbranched alkane chain. For short chains ($<C_4$) the separation is always poor, increasing sharply to a maximum at C_4 - C_6 and then falling off smoothly for longer C chains. Although the maximum is always between four and six CH_2 groups, the exact position may depend on the metal ion; this needs a more thorough investigation.

With branched chains the trend was similar. For 1,6-diamino-2,2,4-trimethylhexane, the retention time for Xe was 6.5 min compared to 8.1 min for the unbranched 1,6-diaminohexane; however, there is an increase by retention time on going from 1,9-diaminononane to bis-(4-aminophenyl)methane and bis-(4-aminocyclohexyl)methane, in accordance with previous findings³ that the cyclohexyl compound is a very effective one, although slightly less so than the 1,4-diaminobutane derivative. Investigations of cycloalkane and phenyl compounds with chain lengths of four to six carbon atoms seem desirable, however, care will have to be taken to maintain an similar amount of flexibility, because there are indications that the properties of the complexes are strongly dependent on it.

DISCUSSION

From the foregoing one may design the optimum polymeric Schiff base complex for use as a solid phase in gas chromatography. It should contain V^{2+} or Cr^{2+} as central ion, a *p*-toluene or *p*-cumene substituent on the methylene group linking the aromatic rings and a C_4 to C_6 *n*-alkane between the nitrogen atoms.

Figs. 5-9 show some results obtained with these complexes. The separation of

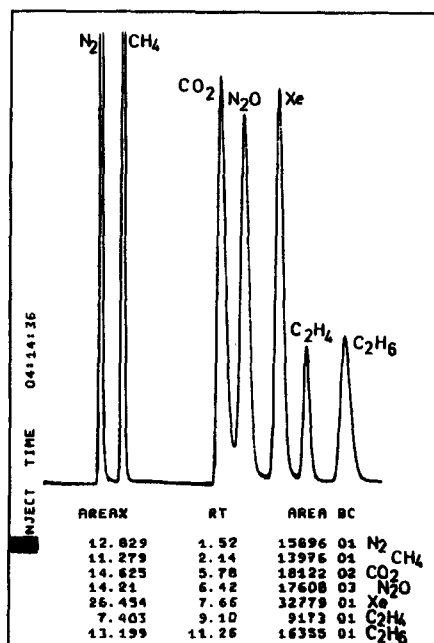


Fig. 5. Separation of a seven-component gas mixture (30 ml He/min, 60°C). Complex: R = *p*-cumenyl, R' = $(CH_2)_6$, M = Ni^{2+} .

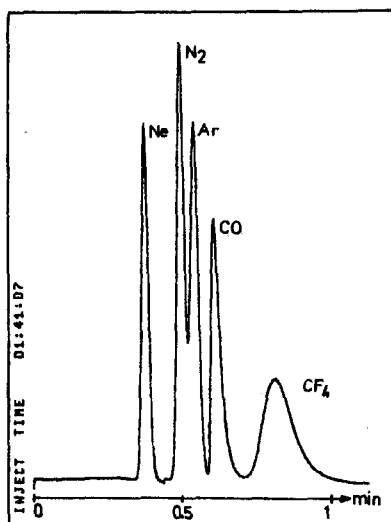


Fig. 6. Separation of Ne, N₂, Ar, CO and CF₄ (40 ml He/min, 20°C). Complex: R = *p*-cumenyl, R' = (CH₂)₄, M = V²⁺.

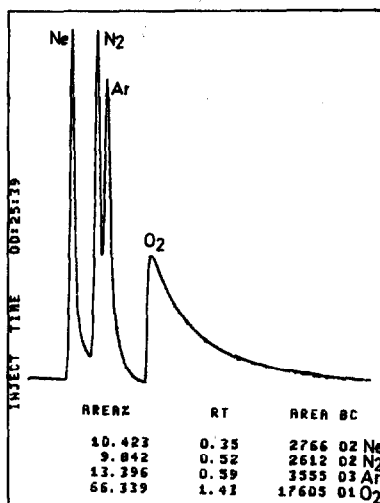


Fig. 7. Demonstration of tailing of oxygen peak by separation of a mixture of Ne, N₂, Ar and O₂ (40 ml He/min, 20°C). Complex: R = *p*-cumenyl, R' = (CH₂)₄, Mn = Cr²⁺.

a number of low-molecular-weight gases is illustrated in Fig. 5. It should be emphasized that the measurement was made with a rather short column at a temperature of 60°C. A special problem is the separation of Ar, N₂, O₂ and CO. Fig. 6 shows the excellent separation of N₂, Ar and CO on the vanadium(II) complex even at room temperature. However, O₂ is chemisorbed on this complex, and this is also true for Cr²⁺, Mn²⁺, Fe²⁺ and Co²⁺ as central ions. Even after saturation of these solid phases with O₂ before measurement, which considerably reduces the overall separation ability, the retention time for O₂ is not constant but dependent on the amount of oxygen in the gas mixture, and the oxygen peak shows heavy tailing (Fig. 7).

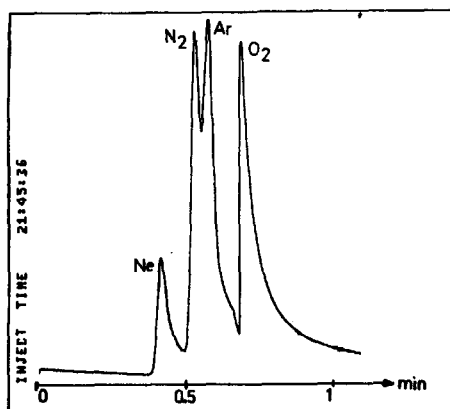


Fig. 8. Separation of Ne, N₂, Ar and O₂. Complex: R = *p*-cumenyl, R' = (CH₂)₄, M = Ni²⁺.

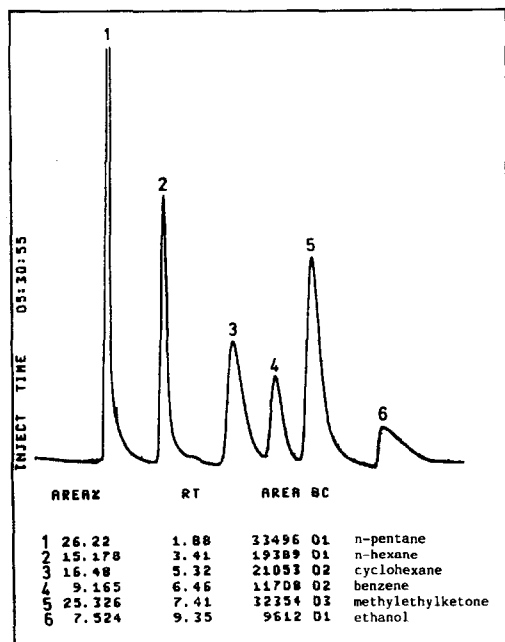


Fig. 9. Separation of a liquid mixture (25 ml He/min, 200°C). Complex: R = *p*-cumenyl, R' = (CH₂)₁₂, M = Ni²⁺.

Therefore, for gas mixtures containing O₂, the nickel(II) complex, which does not react with oxygen, is recommended. Although its separation efficiency is lower than for the complexes of the aforementioned ions, the separation of N₂, Ar and O₂ is satisfactory, the oxygen peak shows a constant retention time and its tailing is reduced (Fig. 8). As the separation efficiency may be improved by using longer columns, these examples show that polymeric Schiff base complexes of the kind described are excellent solid phases for the separation of low-molecular-weight gases.

Fig. 9 shows the separation of a liquid mixture at 200°C. The column efficiency is satisfactory, although the same quality can be achieved with commercially available molecular sieves.

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