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Polymer Benzo[15]crown-5 Complexes as Sensor Materials for Solvent Vapors—Aromatic Halogenated Hydrocarbons and Polar Solvents**

By *Franz L. Dickert** and *Doris Zeltner*

Dedicated to Professor Gerd Wedler on the occasion of his 60th birthday

For the first time thin layers of polymer-metal complexes with crown ether ligands have been applied as sensor materials for the detection of solvent vapors. The hydrophobic properties of these films enable the detection of even halogenated and aromatic hydrocarbons through conductivity measurements.

The crown ether[1] [15]crown-5 (15C5) forms 1:1 complexes with Mg^{II}, Zn^{II}, Co^{II} and Ni^{II} ions (because they fit well into the cavity of this macrocyclic ligand) and can act as a tetra- or pentadentate ligand.[2,3] Complexes with the composition $[M^{II}(15C5)(S)_2]^{2\oplus}$ have been identified in donor solvents (S). In inert solvents, however, even the usually non-coordinating $ClO_4^{\ominus}$ ion yields inner sphere complexes.[3] The reversible substitution reaction of coordinated anions $X^{\ominus}$ (e.g. $ClO_4^{\ominus}$) by donor molecules [Eq. (a)] has been applied to develop sensor materials for solvent vapors:

$$[M^{II}(15C5)(X)_2] + 2\,S \rightleftharpoons [M^{II}(15C5)(S)_2]^{2\oplus} + 2\,X^{\ominus} \qquad (a)$$

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The formation of a charged complex and anions through the interaction of the initial complex with solvent molecules can easily be detected by conductivity measurements. For practical use formaldehyde resins[4] synthesized from benzo[15]crown-5 (B15C5) are more convenient (§B15C5). These polymer materials form complexes with $Mg^{2\oplus}$ such as **1** in $CH_3OH/CHCl_3$ solution.

Solutions of these polymer complexes are dropped onto interdigital structures to perform conductivity measurements. Stable amorphous films with a thickness of approximately 0.2 μm to 1 μm are obtained after evaporation of the solvent.

The sensor effect consists of two steps. First, an absorption of solvent vapors by the solid macrocyclic layers occurs followed by a chemical reaction according to equation (a). Macrocyclic complexes are very favorable materials for the absorption of different kinds of solvent since these ions have pronounced hydrophobic properties. Strong absorption occurs in the case of protic and aprotic polar solvents such as alcohols, ketones, esters etc. and also for aromatic and halogenated hydrocarbons.

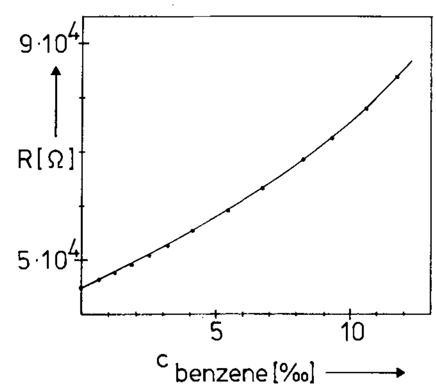


Fig. 1. Dependence of the resistance of the 1:1 complexes of $Mg(ClO_4)_2$ with §B15C5 on an interdigital structure (5 μm electrode distances) on the amount of benzene in the air at 20 °C and 50% humidity.

A typical measurement, e.g. the detection of benzene in the air, is depicted in Figure 1. The resistance of the sensor layers increases parallel with the amount of solvent vapor in the air produced by a gas mixing apparatus.[5] Solvents with no donor properties also result in this sensor effect, since water stemming from the humidity of the air is removed from the sensor layers by the incorporated benzene. Since ionic conductivity is responsible for the described effect, as the ion concentration is diminished according to equation (a) the resistance of the sensor layers increases. The sensitivity of the proposed sensor materials to water vapors can be reduced by increasing the hydrophobic properties of the layers. This can be achieved by the inclusion of cross linking agents such as anisole which enlarge the aromatic ring content in the resins. The addition of ingredients with solvating power such as polyethyleneglycols enables sensors to be designed with characteristic properties. As shown in Figure 2 this procedure can yield a zero slope for certain solvent vapors (e.g. dichloromethane) whereas other solvents (e.g. ethanol) give a sensor response. Ions other than **1** can also be used. The B15C5 ligand acts in the case of the $K^{\oplus}$ ion as a cap since the ion diameter is larger than the cavity dimension of this crown ether. The application of arrays of these sensors with different characteristic lines makes it possible, in combination with the methods of pattern recognition,[6-8] to detect organic vapors in the air independent of the humidity. More generally, the selectivity of these sensors can be improved by sophisticated signal processing.

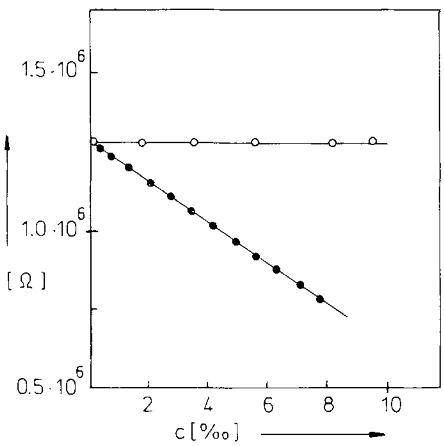


Fig. 2. Dependence of the resistance of the 1:1 complexes of KCl with § B15C5 after the addition of polyethyleneglycol (100 wt.-%, M_r 1000) on an interdigital structure (5 μm electrode distances) on the amount of dichloromethane (○) and ethanol (●) in the air at 20 °C and 30% humidity.

These gas phase measurements can also be applied to detect traces of organic solvents in water. For this purpose a Teflon membrane was applied to separate the sensor element in the gas phase from the water. The solvent vapor is able to penetrate the membrane and a constant vapor pressure of water is obtained in this way. Results for ethanol and dichloromethane are presented in Figure 3. The absorption of the coordinating ethanol [eq. (a)] leads to a decrease in the resistance whereas the opposite effect is observed for dichloromethane as already described for benzene (Fig. 1).

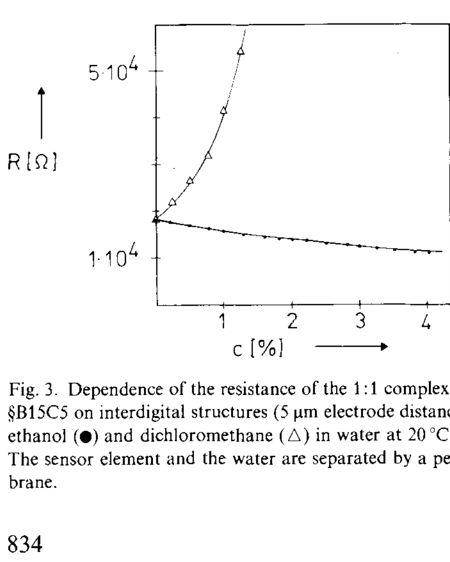
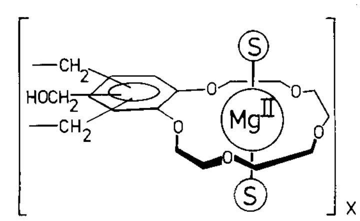


Fig. 3. Dependence of the resistance of the 1:1 complexes of $Mg(ClO_4)_2$ with §B15C5 on interdigital structures (5 μm electrode distances) on the amount of ethanol (●) and dichloromethane (△) in water at 20 °C for a dipping sensor. The sensor element and the water are separated by a permeable Teflon membrane.

The detection limits can easily be determined from the characteristic lines. According to Figure 1, 17 ppm benzene in air or 40 ppm ethanol and 6 ppm dichloromethane in water (Fig. 3) are detectable if a resolution of 10^{-3} for the relative changes in the resistance are assumed.

It is possible to construct low cost equipment for the detection of solvent vapors based on the proposed polymer macrocyclic complexes **1**. The conductivity measurements are easily performed with oscillator circuits incorporating a free running multivibrator. Another possibility is the application of a chemical field-effect transistor (ChemFET).[9] In this method the sensor material is applied to the gate of a ChemFET and electrical contact is realized throuh the use of a perforated electrode[10] which is permeable to gas. In this way compatibility to integrated circuits can be achieved.



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