

EFFECT OF MOBILE PHASE COMPOSITION ON THE SELECTIVITY OF CHROMATOGRAPHY COLUMNS WHICH USE POLYPYRROLE AS THE STATIONARY PHASE

by
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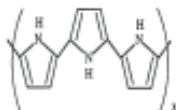
ABSTRACT

Chromatography columns packed with polymeric stationary phase have been prepared. The packing materials were prepared by depositing polypyrrole chloride or polypyrrole dodecylsulfate onto silica particles. The deposition was accomplished by chemical oxidative polymerisation. Chromatographic selectivity of the columns was examined under reversed-phase condition using pairs of test compounds with known functionalities as the probes. The results showed that if hydrophobic interactions were dominant, the selectivity increased with decreasing in organic fraction in the mobile phase, and vice versa.

I. INTRODUCTION

Since the discovery of highly conducting polymers by successfully doping polyacetylene by Shirakawa in 1977 [1], the field of conducting polymers has grown rapidly. Many of these new polymers are derived from pyrroles, thiophenes, and, later, anilines.

The polymers can be prepared by chemical or electrochemical oxidative polymerisation of the monomers. Polymers with a great variety of properties can be prepared by resorting to synthesis conditions including the choice of solvents and monomers, additive added, supporting electrolytes, the nature of the dopants, the electrodes used, as well as the final preparation technique [2,3,4,5,6,7].



Polypyrrole

In the previous report [8] the author presented his study on the polypyrrole based polymers prepared by chemical oxidative polymerization used for the preparation of stationary phases of chromatography columns. Chromatographic characterization and evaluation of the polymer properties were presented emphasizing on hydrophobicity parameter determination. In this report the author discusses similar study (in term of chromatographic characterization), but the particular emphasis is laid on the effect of the mobile phase composition on the selectivity of chromatographic columns. The columns under investigation are the same as before, i.e. the ones packed with polypyrrole-chloride and polypyrrole-dodecylsulfate-coated silicas.

II. EXPERIMENTAL

A. Reagents and Materials

All reagents were of analytical reagent grade unless otherwise indicated. Pyrrole (Fluka, LR grade) was distilled before used. Methanol (HPLC grade, BDH) and Milli-Q water were used for preparing the mobile phase. Sodium dodecylsulfate (SDS) was purchased from SIGMA, and FeCl_3 was from BDH. Solution of benzene, toluene, phenol, aniline, diethylphthalate (DEP), and dimethylphthalate (DMP) were prepared in the mobile phase at concentrations required for good detection.

Silica (Ultrasphere, Beckman) for stationary phase preparation was used as received. The silica has 10 mm particle size, 220 m^2/g surface area, and 80 Å pore size. Stainless steel columns (4.9 x 50 mm) were purchased from Altech.

B. Instrumentation

Chromatographic analysis was carried out using an HPLC system consisting of a Dionex basic module with a built-in 50 ml sample loop injector, a ERC 7210 variable wavelength detector (Erma), and a DP 600 chart recorder (ICI).

C. Column Preparation

Polypyrrole chloride and polypyrrole dodecylsulfate were coated onto silica particles and used as the column packings. Chemical oxidative polymerisation was employed to prepare the packing materials which were then packed into the columns by slurry packing method. The column packed with polypyrrole chloride was designated as PPCl/Si, while the one packed with polypyrrole dodecylsulfate as PPDS/Si.

D. Chromatographic Measurements

The columns were flushed with water and methanol before use. A methanol-water system was used as the mobile phase, the composition of which was varied as required. The mobile phase flow rate was held constant at 1 mL/min throughout the measurements. The eluent output was monitored at 254 nm. Retention times were recorded using a stopwatch, and the dead-time (t_0) was determined from the retention time of water.

III. RESULTS AND DISCUSSION

The selectivity of a chromatographic column is a function of the thermodynamics of the mass-transfer process and this is an important experimental probe in studies of the solute retention process. It can be expressed as:

$$\log \alpha = \Delta(\Delta G^\circ) / RT$$

This reflects the difference between two solutes in the Gibbs free energy transfer from the mobile phase to the stationary phase. Selectivity can indicate differences in the different stationary phases if the same mobile phase composition is used when comparing different stationary phases [9]. This suggests that the selectivities measured for different stationary phases using a pair of solutes with the same mobile phase composition should be very similar [10,11]. In the following discussion five pairs of test samples were used to examine the selectivity behaviour of polypyrrole chloride and polypyrrole dodecylsulphate used for the stationary phases.

The selectivity variation of the toluene-benzene pair with methanol content in the mobile phase is shown in Figure 1. The pair reflects the hydrophobic selectivity available and the variation of this selectivity is more noticeable on PPDS/Si. The results show that the selectivity tends to increase with increasing water content in the mobile phase, as is expected if hydrophobic interactions are dominant. This behaviour is more pronounced on PPDS/Si indicating that PPCl/Si is more polar.

The selectivity profile for the pair phenol-benzene as the mobile phase composition was varied is presented

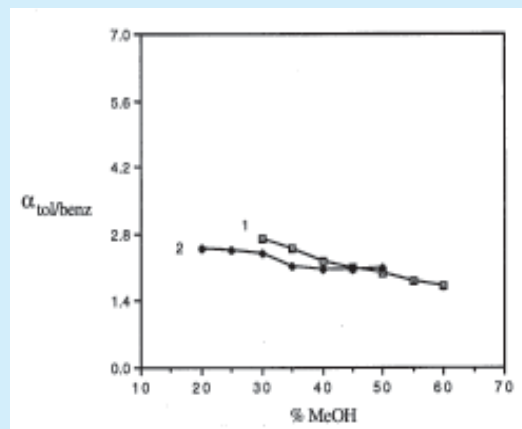


Figure 1
Selectivity variation of the pair toluene-benzene with methanol content in the mobile phase. (1) PPDS/Si, (2) PPCl/Si

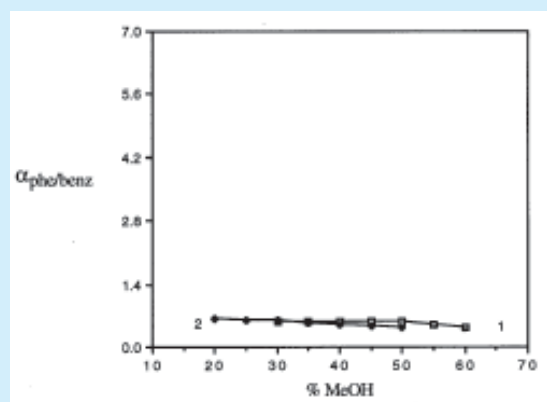


Figure 2
Selectivity variation of the pair phenol-benzene with methanol content in the mobile phase. (1) PPDS/Si, (2) PPCl/Si

in Figure 2. This pair reflects selectivity arising from hydrogen bonding because phenol is capable of being a proton donor. However, as can be seen in the selectivity profile, this type of selectivity does not seem to alter with the variation of the mobile phase. Similar behaviour was observed with both polymers. Being a proton-donor compound, phenol could interact with the mobile phase which was methanol-water system. Both the mobile phase components are capable of acting as proton acceptor with water being stronger [12]. The proton donor-acceptor interactions between phenol and the mobile phase increased as the organic fraction of the mobile phase decreased, resulting in higher contribution of this interaction in reducing the retention of phenol. This effect was, however, compensated by the increase in hydrophobic effect as the water fraction increased. Thus the retention of phenol on both column was mainly determined by solvent effect. The fact that the selectivity for both columns toward the pair phenol-benzene were similar and almost constant indicated that there was no specific interaction involving polar groups in phenol with ones in both columns.

The selectivity behaviour for a pair of compounds having very different properties is shown in Figure 3. Both compounds are polar, however the aniline is an electron donor or proton acceptor, whereas phenol is a pro-

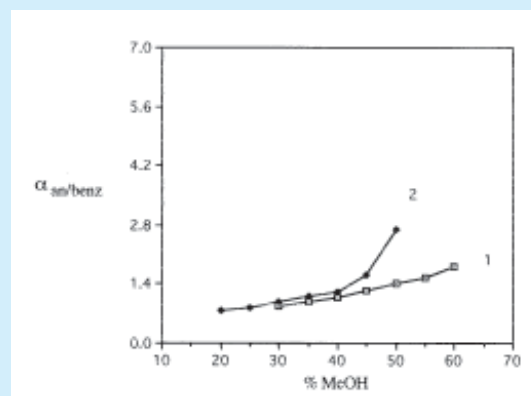


Figure 4.
Selectivity variation of the pair aniline-benzene with methanol content in the mobile phase.
(1) PPDS/Si, (2) PPCI/Si

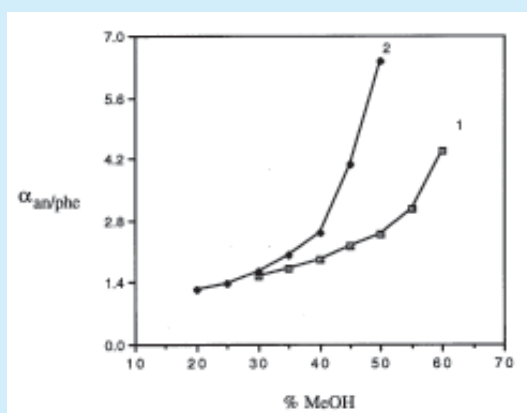


Figure 3
Selectivity variation of the pair aniline-phenol with methanol content in the mobile phase.
(1) PPDS/Si, (2) PPCI/Si

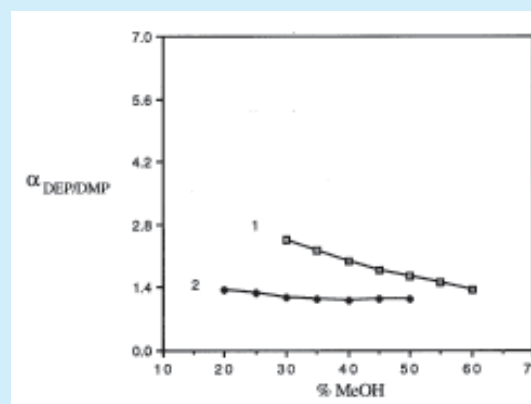


Figure 5
Selectivity variation of the pair DEP-DMP with methanol content in the mobile phase.
(1) PPDS/Si, (2) PPCI/Si

ton donor. One would expect, therefore, that the pair would show significant selectivity. As can be seen in Figure 3, this postulation is verified here with the selectivity increasing with increasing methanol content in the mobile phase. The trend is shown by both columns but it is more pronounced on PPCI/Si. During polymerisation, electron were removed from pyrrole systems resulting in polymeric structure deficient in electrons, hence generating more polar systems (Lewis acid-like systems which are capable of interacting with electron-donor compounds). In the aqueous-organic mobile phase systems, i.e. in the reversed-phase mode, the polar interactions manifested themselves more strongly with the increase in organic fraction. Therefore, aniline, being an electron-donor compound, interacted relatively more strongly in this condition with the polymer. In the water-rich environment, this kind of interaction was negligible because the dominant hydrophobic effects took over the role in the solute-stationary phase interactions. The polar interactions just mentioned were not as strong in the case of PPDS/Si, probably because its higher hydrophobicity due to the incorporation of DS⁻ counterions in the polymer matrix, and that the presence of long alkyl chains of DS⁻ counterions reduced the chance for the aniline to interact with the polymer backbone.

The selectivity behaviour of aniline is further supported by the pair aniline-benzene as seen in Figure 4. Here again, the retention of aniline relative to benzene increased with methanol content in the mobile phase. This argument, however, does not necessarily rule out other possibilities, i.e. interactions involving silanophilic groups from the silica support. The fact that silanophilic interactions increase with organic content in the mobile phase has been reported by other workers [13, 14, 15]. At low organic content the water masks or hydrates the silanolic sites extensively reducing its chance to interact with solutes. These hydrated sites are demasked at high organic content resulting in the increase in silanophilic interactions. In PPDS/Si the silanol groups are probably more effectively shielded by the presence of dodecylsulfate counterions which have long alkyl chain.

The variation of the selectivity of the pair DEP-DMP when the mobile phase composition was varied is shown in Figure 5. Having carbonyl groups in their structure, both compounds are polar but neutral. The side chains containing these polar groups, as well as the alkyl groups at the outside ends, are positioned meta to each other rendering the polar groups less accessible for interaction with the stationary phase. It is reasonable, therefore, to

assume that separation is based on the differences in hydrophobicity due to the difference in the length of alkyl side chains they contain. The selectivity on PPDS/Si increased with increasing water content in the mobile phase, typical of hydrophobic selectivity. On PPCI/Si, however, the selectivity was almost unchanged indicating that separation on the basis of hydrophobicity of the solutes was less favourable.

IV. CONCLUSION

From the study of solute retentions under different mobile phase compositions some points can be observed :

1. Polar interactions become more dominant at higher methanol concentrations in the mobile phase (typically > 40%),
2. At the lower methanol concentrations hydrophobic interaction become more pronounced,

The increase in polar selectivity at higher methanol concentrations is probably due to the silanol groups becoming more accessible as the stationary phase become more wetted. The increase in polar selectivity with increasing methanol content, however, could also be due to the genuine specific interactions of the solutes and the stationary phase itself. The changes from polar-interaction-dominated range to hydrophobic-interaction-dominated range is slower on PPDS/Si.

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