CHROMATOGRAPHIC CHARACTERISATION OF POLYPYRROLE-BASED CONDUCTIVE POLYMER

by

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ABSTRACT

A chromatographic study on the properties of polypyrrole-based conductive polymers has been carried out. The polymers were chemically oxidatively prepared and coated directly onto silica particles and packed under high pressure into stainless steel chromatography columns. A series of small molecules were used as test compounds and chromatographic measurements were performed under reversed phase condition. The study revealed the properties of the polymers, such as their hydrophobicity, which were deduced from their behaviour in the interactions with the test compounds.

I. INTRODUCTION

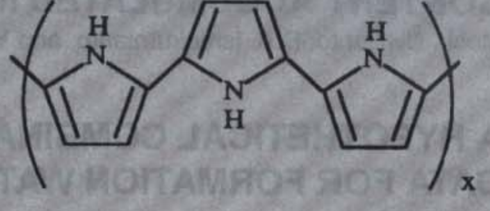
A conductive polymer is an organic polymer that has electrical, electronic, magnetic, and optical properties similar to those of a metal in addition to the other properties commonly associated with a conventional polymer. As a group, conductive polymers have one thing in common: all of them contain extended π-conjugated-systems, single and double bonds alternating along the polymer chain [1].

Many of these new polymers are derived from pyrroles and thiophenes, a wide variety of which have been found to polymerise when oxidised either chemically or electro chemically [2]. The polymers become conductive only if they are in a "doped" state which can be achieved by oxidation (p-doping) or reduction (n-doping) [3]. In the case of polyaniline, however, the doping can also be carried out by protonation of the imine nitrogen [4].

Since the discovery of highly conducting organic polymers by successfully doping "Shirakawa" polyacetylene in 1977 [5], the field of conducting polymers has grown rapidly. It was catalysed by the promise that this new class of polymers could act as a synthetic replacement for metal in many applications.

The polypyrrole system (shown below) has attracted considerable attention and has been subjected to extensive studies. The attractiveness of this conductive polymer comes from several factors: their chemical and thermal stability[5, 6], polymers with a great variety of properties can be produced by resorting to derivatives[2,7], copolymers[8,9], or incorporation of particular anions [10, 11] during synthesis.

In this report the author presents his study on the chromatographic characterisation of two kinds of conductive polymer, i.e. polypyrrole chloride and polypyrrole dodecylsulfate. These materials were coated onto silica gel particles and packed into chromatography columns. A series of small molecules with known functionalities were used as molecular probes to test the interaction capabilities of these polymeric materials.



Polypyrrole

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 employed for preparing the mobile phase. Sodium dodecylsulfate (SDS) was purchased from SIGMA, and $FeCl_3$ was from BDH. Solution of benzene, toluene, phenol, aniline, N-N-dimethylaniline (DMA), diethylphthalate (DEP), and dimethylphthalate (DMP) were prepared in the mobile phase at concentrations the levels of which were depending on the amount required for 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 characterisations were performed using an HPLC system consisting of a Kortec K350 pump (ICI) connected to a Rheodyne 7125 injector with 20 µl sample loop or a Dionex basic module with a built-in 50 µl loop injector; a ERC 7210 variable wavelength detector (Erma); and a DP 600 chart recorder (ICI).

C. *Preparation of Column Packings and Columns*

Silica particles coated with polypyrrole chloride and polypyrrole dodecylsulfate were used as column packings. These packings were prepared employing chemical polymerisation technique. The chromatography columns used in this study were packed with either one of those two kinds of packings. The column packed with polypyrrole chloride was designated as PPCl/Si, while the one packed with polypyrrole dodecylsulfate as PPDS/Si. Details of the preparations of column packings and the columns have been described elsewhere [12].

D. *Chromatographic Measurements*

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

III. RESULT AND DISCUSSION

There is a linear relationship between log k' and the organic fraction as expressed in equation (1),

$$\log k' = \log k_w - S\varphi \qquad (1)$$

where φ is the volume fraction of the organic modifier in the mobile phase, *S* is the slope, and $\log k_w$ is the intercept obtained by extrapolating k' to pure water mobile phase. It has been shown[13, 14] that the $\log k_w$ value is closely related to log P, the logarithm of the partition coefficient which expresses the equilibrium of a solute between an organic (n-octanol) and an aqueous (water) phases. This parameter has been widely accepted as a measure of solute hydrophobicity[15, 16]. On the other hand, the value of $\log k_w$ is a measure of the retention of a solute if pure water is used as the mobile phase, at which condition the hydrophobic interaction is dominant.

Many workers have investigated the usefulness of the technique and the applicability of various columns to predict solute hydrophobicity in efforts to replace the shake-flask method (for log P measurement) which is tedious and time consuming[15, 17, 18]. A reasonable success for octadecylsilane (ODS) columns for this purpose could be attributed to the similarity in the interphase system existing in these columns, if methanol-water mobile phase system is used, and that of octanol-water system is employed for log P measurement [13]. According to Chen et al[19] the intercept of the log k' - φ plots, i.e $\log k_w$, is determined mainly by the properties of the stationary phase. Relating these two parameters to each other, therefore, may reveal how a stationary phase interacts with a solute under specified conditions, which, in turn reflects the properties of the phase and allows prediction of the solute hydrophobicity.

In Table 1 the values of the correlation coefficients, *r*, for the plots of log k' against φ calculated for each test compound for PPCl/Si and PPDS/Si are presented. As can be seen, very good correlation ($r > 0.99$) for the plots of log k' against φ are obtained in all cases indicating that extrapolation to pure water to measure $\log k_w$ is reasonable.

The $\log k_w$ values for PPCl/Si and PPDS/Si are presented in Table 2 together with the ones for a Lichrosorb RP-C_{18} obtained from the literature [17]. The standard hydrophobicity parameter values, i.e log P, of the compounds[20] are also included for reference.
It can be seen that the orders of $\log k_w$ values for RP-C_{18} and log P from benzene to DMA are the same, i.e in the series toluene> DMA > benzene > phenol > aniline, indicating they are closely related to each other. This suggests that the interactions or partition processes between two phases in each system have similarities. For the same

Table 1
The values of correlation coefficient (*r*) of the plots of log k' against φ for individual test compound for PPC1/Si and PPDS/Si

Test compound	*r*	
	PPCl/Si	PPDS/Si
Benzene	0.995	0.997
Toluene	0.998	0.999
Phenol	0.997	0.990
Aniline	0.997	0.994
DMA	0.996	0.999
DMP	0.992	0.999
DEP	0.997	0.999

Table 2
The values of log k_w for PPCl/Si, PPDS/Si and RP-C_{18}, and log P

Test compound	Log k_w			Log P^b
	PPCl/Si	PPDS/Si	RP-C_{18} ^{a}	
Benzene	1.09	1.12	2.08	2.13
Toluene	1.57	1.75	2.62	2.73
Phenol	1.01	1.00	1.23	1.46
Aniline	0.72	0.74	1.13	0.90
DMA	2.02	2.08	2.36	2.31
DMP	1.50	2.15	n.a	n.a
DEP	1.67	2.80	n.a	n.a

a. from ref. 17
b. from ref 17, 20

series of solutes the orders of log k_w values for PPCl/Si and PPDS/Si are the same, i.e in the series DMA> toluene > benzene > phenol> aniline. They are, however, different from both the series in log P and log k_w values of RP-C_{18}, indicating that there are differences in separation mechanisms or solute interactions with these stationary phase systems.

Between PPCl/Si and PPDS/Si themselves an important difference is also noticeable. The log k_w values for DMP and DEP are significantly lower on PPCl/Si compared with that obtained on PPDS/Si. Furthermore, these values on PPCl/Si are similar to those obtained for toluene, while on PPDS/Si they are significantly higher. DMP and DEP have carbonyl groups which are polar and act as hydrogen bond acceptors. Water, on the other hand, is a strong hydrogen-bond donor. The interactions between these opposite groups might reduce the intensity of the hydrophobic interactions between DEP or DMP with the stationary phase. In the pure water environment (log k_w), the hydrophobic effect was the main driving force for the interactions to occur between the solutes and the stationary phase. The fact that the influence of the polar groups in DMP and DEP in decreasing the retention was more pronounced on PPCl/Si confirms that this column is less hydrophobic than PPDS/Si. It is also shown that log k_w values for benzene and toluene, both hydrophobic compounds, as measured by extrapolation, are significantly lower on PPCl/Si and PPDS/Si compared with that obtained on RP-C_{18}. This suggests further that both polymeric columns are less hydrophobic than RP-C_{18}, at least in the theoritically pure water system.

It has been proposed previously that relating the values of the hydrophobicity parameter measured in one system to that from other system can provide information on the similarity or differences in the interaction or separation mechanism involved in each system[17, 18]. This principle was applied here to compare PPCl/Si with PPDS/Si by plotting log k_w values for PPCl/Si against those for PPDS/Si. The result is presented in Figure 1

According to Minick et al[18] and Melander et al[21] equations correlating two sets of hydrophobicity parameter values represent a linear-energy relationship in which the slope is an estimate of how closely the free energies of the processes compare. The slope of the regression equations obtained here is 1.4031 and the correlation coefficient is 0.846. The relatively large deviation from unity in the slope and relatively low correlation coefficient indicate that the physical processes governing the separation mechanisms in each column system were different. Since the mobile phase systems used for log k_w measurements were the same, the variation in separation mechanism arose from differences in the stationary phases. Both polymeric phases have the same polymer backbone, i.e polypyrrole. On PPDS/Si, however, the polymer contains long alkyl chains from the surfactant ions of dodecylsulfate. The hydrophilic ends of the chains which bore negative charge are probably oriented towards the polymer chains. The polymer would, therefore, show hydrophobic character. The existence of the long alkyl chain moities in the polypyrrole matrix would change the interaction behaviour of the parent polymer with the surrounding system.

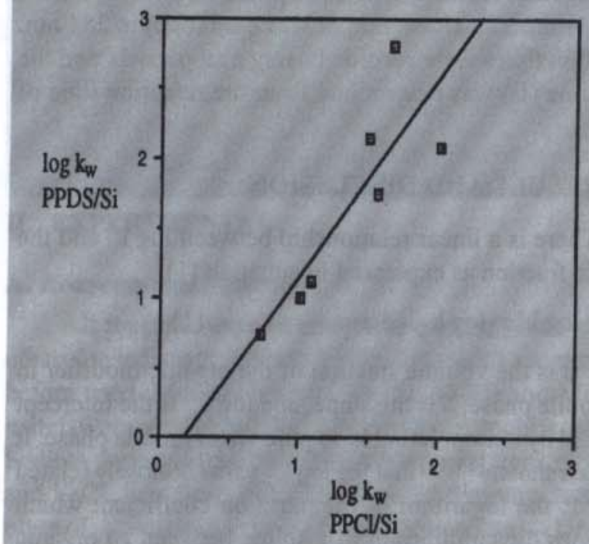


Figure 1
The relationship between log k_w values for PPC1/Si and PPDS/Si obtained by linear approximation.
y = - 0.25735 + 1.4031 X   r = 0.8460

Chen et al[22] found that the slopes of the plot, *S*, for a particular solute using the same mobile phase system were almost constant for similar columns, in this case C_{18} columns.They further proposed that any variation in *S* reflected the difference in retention mechanisms between the solutes and the stationary phases which could be due to mixed-mode interactions such as the involvement of silanophilic interactions. Based on the points just discussed, it is then reasonable to consider that if two columns packed with very different packing materials are compared with each other, their *S* values should accordingly not be the same if measured with the same solute and the same mobile phase system.

In Table 3 the values of *S*, the slope of log k' - φ plots, for PPCl/Si and PPDS/Si are presented together with that for C_{18} columns from the literature for comparison. It can be seen that the *S* values vary among the columns considered. The variation in *S* values suggests that the interactions or separation mechanisms for the solutes are not the same. This reflects differences either in the type of the stationary phase material or in the degree of interactions between the solutes and the underlying silica. Because the slope shows the effect of changes in mobile phase composition on the solute retention, this will also reflects changes in the physical conditions of the stationary phase as a function of the mobile phase. For example, it is known that the structure of the alkyl chains in bonded phases is dependent on mobile phase composition [23, 24].

It is also an interesting point that if one compares the average value of *S* and its variation for the whole set of solutes for PPCl/Si to that for PPDS/Si, the variation of the average value of *S* is 17.8 % for PPCl/Si, while it is 31.9 % in the case of PPDS/Si. This significant difference might suggest that the role of solute interactions on the retention was less pronounced on PPCl/Si when compared to that on PPDSISi. This may further indicate that PPDS/Si could offer better selectivity than PPCl/Si if used as chromatographic stationary phase. This may also suggest that PPDS/Si was more multifunctional.

Table 3
The values of *S* for PPCl/Si, PPDS/Si, and various C_{18} columns

Test compound	*S*			Average
	PPCl/Si	PPDS/Si	C_{18}^{a}	
Benzene	3.27	2.55	2.76	2.86 ± (12.94%)
Toluene	3.67	3.21	3.28	3.39 ± (7.32%)
Phenol	3.83	2.89	2.9	3.00 ± (25.84%)
Aniline	2.05	1.48	2.13	1.89 ± (18.78%)
DMA	3.41	2.85	3.09_{b}	3.12 ± (9.01%)
DMP	3.34	3.73	n.a	3.54 ± (5.52%)
DEP	3.62	4.60	n.a	4.11 ± (11.92%)
Average	3.31 ± (17.8%)	3.04 ± (31.9%)		

a) from ref. 22
b) from ref. 19

IV. CONCLUSIONS

Two kinds polypyrrole-based polymers have been prepared and their properties have been investigated chromatographically. The results of the study suggest that the polymers can not be used to determine solute hydrophobicities chromatographically. The results obtained were too low, for the test compounds examined, when compared with those of standard values.

Both polymers have the same molecular backbone, i.e. polypyrrole. The incorporation of surfactant ions into one of them, but not into the other, made indicatively their interaction behaviour with the test compounds not the same. The polymer containing surfactant ions seemed to be more hydrophobic and have better selectivity which might be due to being more multifunctional.

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