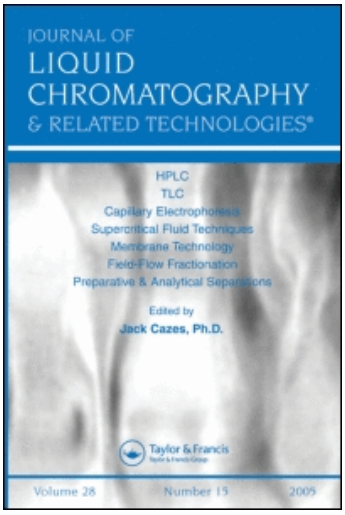

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CHROMATOGRAPHIC STUDY OF INTERACTIONS BETWEEN N,N-DISUBSTITUTED POLYACRYLAMIDES AND PHENOLS COMPARISON WITH INFRARED SPECTROSCOPIC DATA.

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ABSTRACT

The determination of retention data by liquid chromatography (LC), for a series of p-substituted phenols on various packings formed with N,N-disubstituted polyacrylamides, permits characterization of polymer-solute interactions which govern the partition of phenols between the mobile and the stationary phases. The partition coefficient, K_i, changes with the nature of the polymer, and increases with the phenolic acidity. We propose a linear relationship between K_i and the complexation constant of phenol-amide hydrogen bond, determined by infrared spectroscopy. This relationship has been qualitatively checked.

INTRODUCTION

For many years, chromatographic techniques have been proposed to characterize polymer-"small molecule" molecular interactions. For that purpose, the polymer is used as stationary phase. The retention volume for a solute increases as its interaction with the stationary phase (the polymer) is increased the measurement of retention data for identical chromatographic conditions, leads to the estimation

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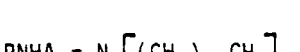
of stationary phase-solute interaction.

This method was first used with gas chromatography ([1-4]) to measure the Flory-Huggins' interaction parameter. However, this technique is limited to polymers which are liquid at the experimental temperature. This limitation does not exist in liquid chromatography whenever a solvent that swells the polymer is used. We first determined how to fix the polymer to an inert support and then examined the influence of flow rate and injected quantity. Finally, we calculated polymer-small molecule classical thermodynamic parameters from the chromatographic data.

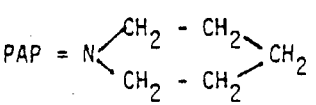
We have tested this general methodology by studying the chromatographic retentions of a series of p-substituted phenols (I) in carbon tetrachloride on the poly-N,N-dihexylacrylamide (PNHA) and on the polyacrylopiperidide (PAP) as LC stationary phases. The synthesis of these polymers is described elsewhere ([5-7]) :

(I)

Z = CH_3, OHC_3, H, Cl



PNHA = $N\left[(CH_2)_5\ CH_3\right]_2$



PAP = $N(CH_2 - CH_2)_2CH_2$

Solute-stationary phase interactions are characterized, in HPLC, by the phenol partition coefficient, K_i between the mobile and the stationary phases. K_i can be written :

$$V_R = V_o + K_i \cdot V_s \qquad (1)$$

V_o : interstitial volume,
V_s : volume of the stationary phase.

We have compared the polymer-phenol interaction data obtained by HPLC with those determined by infrared spectroscopy ([7]). This

approach allowed us to quantitatively estimated the specific part of hydrogen bonds in the molecular interactions involved in the chromatographic retentions.

PREPARATION OF THE CHROMATOGRAPHIC PACKINGS

Each packing is composed of a film of polymer, cross-linked onto an inert support, so as to avoid a washing away of the stationary phase by the mobile phase. We used a silica support, Chromosorb, acid washed, 100-200 mesh in particle size, from Intersmat ([8]).

Before use, the packing was treated with trimethylchlorosilane to eliminate the silanol groups which are able to induce parasitic retentions. The treated support was suspended in benzene. This solvent contains the polymer and a cross-linking reagent (benzoyl peroxide). Solvent evaporation results in a homogeneous layer of polymer and peroxide on the silica particles. The particles are then heated under nitrogen at 100°C for 15 hours. After this operation the non-cross-linked polymer is washed away by soxhlet extraction in carbon tetrachloride. The amount of cross-linked polymer on the silica particles was determined by thermogravimetry and this impregnation rate is a function of the preparation conditions, more specifically of the ratios :

1 = polymer weight/support weight

2 = cross-linking reagent weight/polymer weight.

We have varied ratio 1 between 0 and 20% and ratio 2 between 0 and 8%. We observed a maximum impregnation rate of 4,4%. By the varying of 1 and 2, it was possible to obtain the same impregnation rate, but with different cross-linking of the network.

INFLUENCE OF SOME EXPERIMENTAL PARAMETERS

- Instrumentation

A Waters liquid chromatograph equipped with an M6000A pump, a U6K injector and an M440 UV detector at 280 nm, was used for these

studies. Each previously described stationary phases was packed in a stainless steel column (2.6 mm I.D., 50 cm length) which was filled in dry mode. All the experiments were performed at ambient temperature, with carbon tetrachloride eluent (Prolabo) dried on molecular sieve.

- Variation of the retention volume with the flow rate

We observed a small increase in the retention volume, V_R with the flow rate, d, of the mobile phase (fig.1). This variation can be explained by the fact that the equilibrium of the solute between the two phases is not reached, because of the dynamic of the chromatographic processes. The extrapolation of the straight line $V_R = f(d)$ for $d = 0$ gave us the limit value V_{el}, corresponding to the equilibrium conditions. We generally used this extrapolated values for V_R.

- Variation of the retention volume with the amount of injected solute

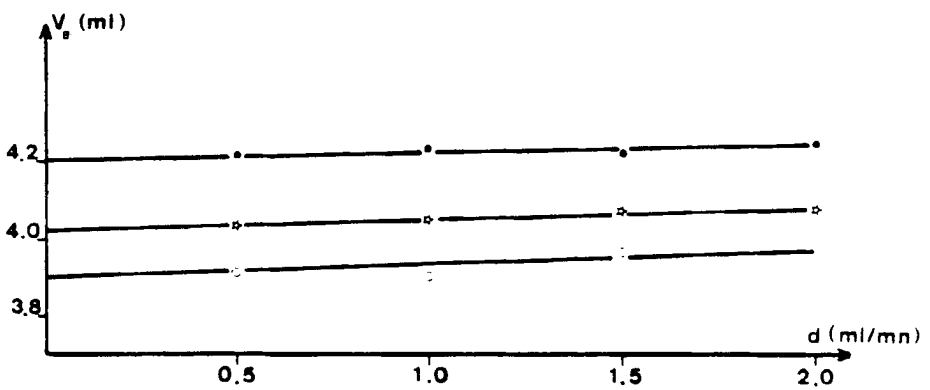


Figure 1 : Variation of the retention volume of phenol versus the flow rate (d) of the eluent (carbon tetrachloride).
Column ; 50 cm x 2.6 mm I.D.
Packing : poly N,N-dihexyl acrylamide cross-linked on chromosorb P.
●: $5\ 10^{-4}$g ; ☆: $2.5\ 10^{-4}$g ; ○: 10^{-4}g.

The partition coefficient, K_i, defined by equation (1), is equal to the ratio C_{is}/C_{im} where :
C_{is} is the solute concentration in the stationary phase ; C_{im}, the solute concentration in the mobile phase.
K_i is not strictly independent of the weight of the injected solute ([9-11]). In our case, we observed a large decrease of V_R by increasing the weight of phenol. However, for a solute injection of less than 10^{-5}g, we no longer noticed variation of the retention volume ; that can be considered as the retention volume for a solute at the infinite dilution conditions. We routinely used these conditions for our measurements.

- Influence of the impregnation rate and degree of cross-linking of the stationary phase

Under our experimental conditions (impregnation rate between 1 and 4,4%), K_i is independent of the impregnation rate and of the degree of cross-linking of the stationary phase. This result shows that, in the conditions used in our work the support does not induce notable parasitic retention.

EXPERIMENTAL RESULTS

The partition coefficient, K_i, is measured from the relationship

$$K_i = \frac{V_R - V_o}{V_s} = (V_R - V_o) \cdot \frac{\rho_s}{m_s}$$

m_s = weight of the stationary phase ; ρ_s = specific weight of the stationary phase, determined by pycnometry. The values of the partition coefficients for several phenols between the mobile phase (carbon tetrachloride) and the stationary phase (poly-N,N-disubstituted acrylamide) are reported in Table 1. These values are average values determined for experiments performed with four different stationary phases (variable m_s).

Measurement reproducibility is excellent, but the evaluation of errors brought about by the various parameters and the necessary extrapolations led us to a precision of about 20% for the K_i values.

DISCUSSION

- Influence of the phenol acidity on the partition coefficient

The affinity of phenols for the stationary phase varies as the corresponding K_i values (Table 1). For the two polymers studied, the order of increasing solute affinity is :

p.methyl phenol < p.methoxy-phenol < phenol < p.chlorophenol < p.cyano and p.nitrophenol. (For the two last phenols, the retention volumes are very large, so they are eluted after a long time and their detection is imprecise). This order is identical to the one obtained when phenols are classified in order of their increasing acidities ([12]) or by their proton donor characteristics ([13-14]). Fig.2 shows the linear relationships we observed, for the two polymers, between log K_i and the pK_a values of the phenols.

- Influence of the nature of the polymeric stationary phase

For all the phenols we studied, their partition coefficients between a poly disubstituted acrylamide and carbon tetrachloride are about five times higher with polyacrylopiperidide (PAP) than with poly-N,N-dihexylacrylamide (PNAH) (see Table 1).

However, in the relationship $K_i = (V_R - V_o)/V_s$, V_s does not represent the volume of the deposited polymer on the inert support, but the volume of the polymer swollen by carbon tetrachloride. Consequently, it is not possible to directly compare the two polymers except if they are swollen in the same manner by the mobile phase.

In the present case, the chemical structures of the two polymers are very similar however the K_i values,higher for the PAP than for the PNAH,are significantly consistent with a stronger interaction with phenol ([7]).

- Relationship between K_i and the complexation constant measured by infrared spectroscopy

Spectroscopic techniques, especially infrared spectroscopy, are now classical methods for studying solute-solvent specific inter-

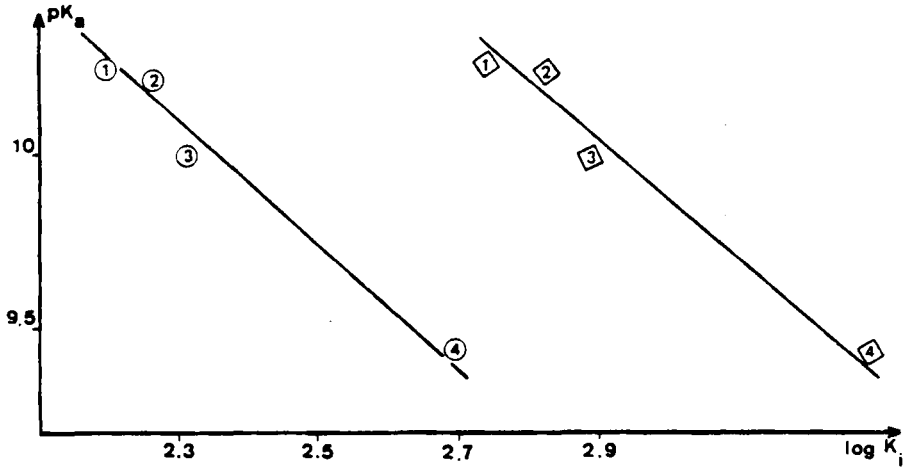


Figure 2 : Relationship between Log K_I and pK_A.
○: poly N,N-hexyl acrylamide ;
◇: polyacrylopiperidide ;
1 : p.methylphenol ; 1 : p.methoxyphenol : 3 : phenol ;
4 : p . chlorophenol.

actions in dilute solution ([15-16]). On the other hand, chromatographic methods provide the possibility to measure global interactions between compounds.

For the systems we have studied, the polyacrylamide-phenol interaction is characterized by a hydrogen bond between the phenol hydoxyl and the carbonyl of the amide function. The study of absorption spectra of the OH stretching vibration ([7]) form dilute solutions in carbon tetrachloride allowed us to calculate hydrogen bond complexation constants which will be compared here with the corresponding K_i values.

- Thermodynamic aspect

In a complexation equilibrium between a proton donor D and an acceptor A, leading to a hydrogen bond complex AD :

$$A + D \rightleftharpoons AD$$

The equilibrium constant can be written :

$$K = \frac{x_{AD} \cdot \gamma_{AD}}{x_A \cdot x_D \cdot \gamma_A \cdot \gamma_D} \qquad (2)$$

x_A, x_D, x_{AD} and γ_A, γ_D, γ_{AD} are, respectively, the molar fractions and the activity coefficients of the corresponding compounds (molar fractions for the polymer are expressed with respect to its monomer unit).

This K constant is the thermodynamic equilibrium constant and is independent of concentration.

By infrared spectroscopy, we have determined ([7]) the "apparent constants" K_1 :

$$K_1 = \frac{x_A}{x_A \cdot x_D} = \frac{\gamma_A \cdot \gamma_D}{\gamma_{AD}} \cdot K$$

The activity coefficients and, as a result, K_1, are dependent upon the concentrations of the present species.

In our spectroscopic experiments, A is one of the poly N,N-disubstituted acrylamides and D, one of the phenols. The phenol concentration is always lower than 5.10^{-3} mole/liter and the activity coefficients of D and AD can then be considered to be equal to γ_D and γ^{∞}_{AD} (phenol and complex activity coefficients taken at infinite dilution). In that case :

$$K_1 = K \cdot \gamma_A \cdot \frac{\gamma^{\infty}_D}{\gamma^{\infty}_{AD}}$$

For a given donor-acceptor couple, the constant, K_1, is dependent upon γ_A, through the acceptor activity coefficient. Because of the absorbance of polyacrylamides in the 3,700-3,500 cm^{-1} range, K_1 can be determined by IR spectroscopy only for low concentrations of polymers (x_A in the range $2\ 10^{-3}$ - 10^{-2}).

In the chromatographic experiments, the same donor-acceptor equilibrium occurs in the stationary phase and the relation (2) takes the form :

$$K = \frac{x_{AD,s} \cdot \gamma_{AD,s}}{x_{A,s} \cdot x_{D,s} \cdot \gamma_{A,s} \cdot \gamma_{D,s}}$$

(subscript s is assigned to species in the stationary phase).

As the quantities of solute D are low, we can consider this constituent as infinitely diluted :

$$K = \frac{x_{AD,s}}{x_{A,s} \cdot x_{D,s}} \cdot \frac{\gamma^{\infty}_{AD,s}}{\gamma_{A,s} \cdot \gamma^{\infty}_{D,s}}$$

This last relationship can be written :

$$\frac{x_{AD,s}}{x_{D,s}} = \frac{(AD)_s}{(D)_s} = K \cdot x_{A,s} \cdot \gamma_{A,s} \cdot \frac{\gamma^{\infty}_{D,s}}{\gamma^{\infty}_{AD,s}} \qquad (3)$$

$(AD)_s$ and $(D)_s$ are the concentrations of the species AD and D in the stationary phase.

We also have to consider the partition equilibrium of the donor between the mobile and the stationary phases :

D (Mobile phase) ⟷ D (stationary phase)

The corresponding constant, in high dilution conditions, is :

$$k = \frac{(D)_s}{(D)_m} \cdot \frac{\gamma_{D,s}}{\gamma_{D,m}} = \frac{(D)_s}{(D)_m} \cdot \frac{\gamma^{\infty}_{D,s}}{\gamma^{\infty}_{D,m}}$$

(subscript m refers to the mobile phase).

Hence :

$$\frac{(D)_s}{(D)_m} = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}} \qquad (4)$$

The basic relationship in liquid chromatography is :

$$V_R = V_o + V_s \cdot \frac{\text{total concentration of the D species in the stationary phase}}{\text{total concentration of the D species in the mobile phase}}$$

As the total concentration of the D species in the stationary phase is $(D)_s + (AD)_s$:

$$V_R = V_o + V_s \cdot \frac{(D)_s + (AD)_s}{(D)_m}$$

or :

$$\frac{V_R - V_o}{V_s} = \frac{(D)_s}{(D)_m} + \frac{(AD)_s}{(D)_m}$$

by expressing the ratios $\frac{(D)_s}{(D)_m}$ and $\frac{(AD)_s}{(D)_m}$ through relationships (3) and (4) :

$$\frac{V_R - V_o}{V_s} = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}} \left(1 + k \frac{\gamma^{\infty}_{D,s}}{\gamma^{\infty}_{AD,s}} \cdot x_{A,s} \cdot \gamma_{A,s} \right)$$

If the polymer concentration in the solutions used for the spectroscopic study is identical to the swollen polymer concentration in the stationary phase : γ_A(relation (2)) is identical to $\gamma_{A,s}$ (relation (3)) and hence :

$$\frac{V_R - V_o}{V_s} = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}} (1 + K_1 x_{A,s})$$

as $K_1 x_{A,s}$ is generally much greater than 1, we can write :

$$\frac{V_R - V_o}{V_s} = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}} K_1 \cdot x_{A,s}$$

In this last relationship, V_s is the volume of the polymer swollen by the eluent. If the densities of the polymer and the solvent are close to each other and if the molecular weights of the solvent and the polymer unit are also close to each other we can combine the weight fraction and the molar fraction of the polymer :

$$\frac{m_s}{\rho_s \cdot V_s} = x_{A,s}$$

(m_s is the polymer weight in the column, ρ_s, its specific weight).

In these conditions, the experimental value :

$$K_i = \frac{(V_R - V_o)}{m_s} \cdot \rho_s$$

determined by liquid chromatography, can be directly correlated with the K_1 value calculated from spectroscopic data :

$$K_i = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}} \cdot K_1$$

This relationship demonstrates that there is a proportionality between the corresponding K_i and K_1 values measured by both methods.

The ratio of the "free" phenol concentrations in the stationary and the mobile phases :

$$k' = \frac{(D)_s}{(D)_m} = k \frac{\gamma^{\infty}_{D,m}}{\gamma^{\infty}_{D,s}}$$

characterizes the interactions other than the hydrogen bond interactions.As a result, the total constant, K_i, measured by chromatography, can be divided into two constants : one characterizing the hydrogen bond interactions (K_i determined by spectroscopy) ; the other k' corresponding to the non-specific molecular interactions :

$$K_i = k' \cdot K_1$$

We have found a relationship close to the ones proposed previously for the comparative study of complexation by spectroscopy and gas chromatography ([1-3]).

- Experimental verification of the K_1 - K_i correlation

The values of the complexation constants K_1 and of the partition coefficients K_i, for the phenol/polymer systems we studied are summarized in Table 1.

TABLE 1

Polymer	Constant	PHENOL p.methyl	p.methoxy	phenol	p.chloro
PNHA	K_1	115	420	420	770
	K_i	120	140	160	390
PAP	K_1	270	450	530	850
	K_i	580	700	830	2,040

Comparison between the complexation constants measured by IR spectroscopy (K_1) and the partition coefficients determined by chromatography (K_i).

From the above calculations, a linear relationship must exist, for a given polymer, between log K_1 and log K_i, if the polymer-phenol interactions different from hydrogen bonds do not depend on the nature of the various phenols. That correlation for the two polymers (fig. 3) is fairly good, except for the p.methyl phenol which has an aberrant behaviour (which is also observed by plotting log K_1 versus pK_A ([5,7]). In all the cases studied, K_1 is greater than k' ; this fact confirms the importance of the hydrogen bond interactions in the chromatographic processes regarding to the Van Der Waals interactions.

CONCLUSION

We have studied the chromatographic behaviour of two N,N-disubstituted polyacrylamides as LC stationary phases, towards various eluted phenols and have shown that, with some experimental precautions, liquid chromatography is a technique which allows us to measure solute/polymer molecular interactions.

In these experiments, the precision of the partition constant determinations remains low but if would be appreciably improved by decreasing the particle size of the packings and by adjusting the column length according to the interactions to be measured.

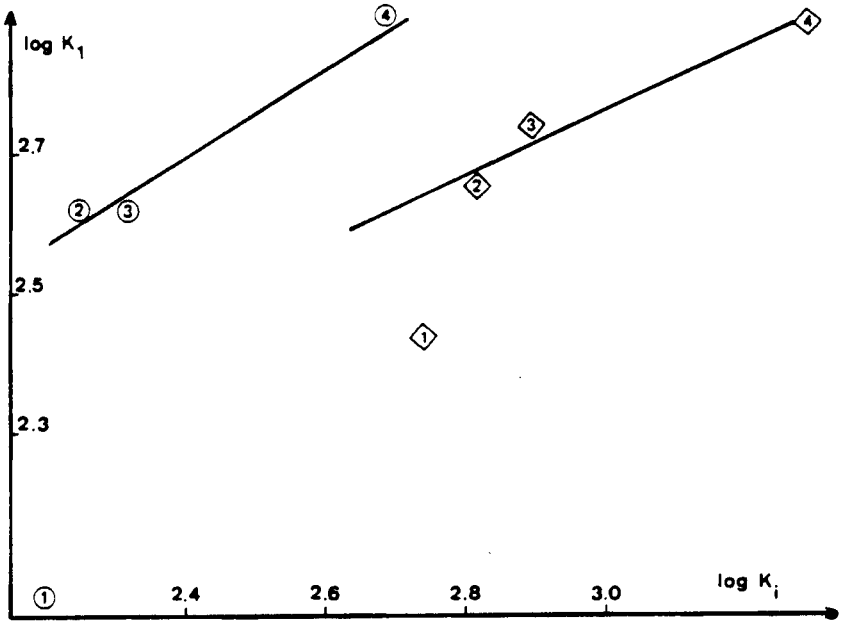


Figure 3 : Correlation between Log K_1 and Log K_i.
○: poly N,N-dihexylacrylamide ;
◇: polyacrylopiperidide ;
1 : p.methylphenol ; 2 : p.methoxyphenol ; 3 : phenol ;
4 : p.chlorophenol.

With some assumptions that have been discussed, the chromatographic partition constants are expressed as products of two factors : one refering to the Van Der Waals interactions, the other corresponding to the polymer/solute hydrogen-bond interactions which are, here, predominant.

We consider that liquid chromatography should also allow us to study polymer/polymer interactions.

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