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CHROMATOGRAPHY OF AROMATIC COMPOUNDS ON CROSS-LINKED POLYVINYLPIRROLIDONE AND ON ANION-EXCHANGE RESINS

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SUMMARY

The distribution coefficients of a large number of chlorinated phenols and phenolic compounds containing two aromatic nuclei have been determined on cross-linked polyvinylpyrrolidone and on anion exchangers in the acetate form. Solutes with low affinity for polyvinylpyrrolidone have been separated in 1 mM hydrochloric acid, while 3-7 M acetic acid has been used for chlorinated compounds. Acetic acid is a suitable eluent in chromatography on anion exchangers. Hydrogen bonding of phenolic protons to the resins, together with non-polar interactions, are mainly responsible for the sorption on both of these types of resins. Under the applied conditions, the relative importance of hydrogen bonding is greater for polyvinylpyrrolidone than for the anion exchanger.

INTRODUCTION

Chromatography in aqueous media on cross-linked polyvinylpyrrolidone¹ (PVP) and on anion exchangers in the acetate form²⁻⁴ gives effective separations of a large number of benzene derivatives containing phenolic hydroxyl groups and carboxylic acid groups. Current studies of effluents from the wood-pulp industry have made it necessary to extend these studies to compounds containing two aromatic nuclei and different types of aliphatic side chains, and to also include chlorinated compounds.

EXPERIMENTAL

Chromatographic separations (1-10 μ g of each compound) were made in aqueous media on two strongly basic anion-exchange resins in bead form, Dowex 1-X8 (17-20 μ m) (Dow Chemical, Midland, Mich., U.S.A.) and Aminex A-28 (8-12 μ m) (Bio-Rad Labs., Richmond, Calif., U.S.A.), and on cross-linked polyvinylpyrrolidone (Polyclar AT (60-75 μ m), crushed particles, General Aniline and Film Corp., New York, N. Y., U.S.A.). The experimental conditions were similar to those used previously¹⁻⁴. The volume distribution coefficient, D_v , was calculated from the peak

elution volume (\bar{v}) by use of the equation $D_b = \bar{v}/X - \epsilon_I$, where X is the bed volume and ϵ_I is the relative interstitial volume. Except for the experiments with carboxylic acids in pure water and in 1 mM hydrochloric acid, the peak elution volumes were reproducible to within $\pm 1\%$ or better and the peak areas to within $\pm 1.5\%$.

Most of the compounds referred to in Table II and Figs. 2 and 4 were supplied by Dr. Knut Lundqvist, Institute of Organic Chemistry, CTH, Göteborg; the remaining compounds were obtained from commercial sources.

RESULTS AND DISCUSSION

Influence of the eluent composition

In agreement with the results reported previously, non-symmetric peaks were obtained when carboxylic acids were eluted on PVP in pure water¹. The few D_b values reported for pure water in this and in the previous paper should therefore not be regarded as true distribution coefficients but rather as the adjusted retention volume (in column volumes) under the experimental conditions.

In order to study the possible effect of contributions of ion exchange to the sorption, experiments were made with different eluents (Table I). As expected, the retention volumes of the two solutes which lacked carboxylic acid groups were only slightly affected by an increase in the hydrochloric acid concentration from zero to 0.02 M. On the other hand, the addition of sodium chloride resulted in a marked increase in retention which can be ascribed to a salting-out effect. The salting-out parameter k_s , defined as the logarithm of the ratio of D_b in 1 M sodium chloride, to that in dilute hydrochloric acid, is 0.17 for phenol and 0.18 for dihydroconiferyl alcohol. A calculation using the data for the retention on a pellicular polyamide resin⁵ gives the value $k_s = 0.17$ for phenol. The same value was obtained⁶ in studies on liquid-liquid distribution at 25°. The results indicate that the conditions inside the resin phase are hardly affected by the presence of sodium chloride in the external solution, and that salting-out parameters can be used for approximate calculations of the effect of salts on the retention values of non-electrolytes.

The results obtained with the carboxylic acids show that PVP behaves like a

TABLE I
VOLUME DISTRIBUTION COEFFICIENTS IN HYDROCHLORIC ACID AND WATER
ON PVP AT 30°

t = Tailing.

Compound	Eluent			
	Water	0.001 M HCl	0.02 M HCl	1 M NaCl in 0.001 M HCl
Phenol	4.8	4.96	4.94	7.30
Dihydroconiferyl alcohol (9)	4.2	4.31	4.37	6.56
2-Hydroxybenzoic acid	>100	68 (t)	12.4	9.17
4-Hydroxybenzoic acid	35 (t)	31.1	30.8	48.2
Dihydroferulic acid (23)	9.8	7.77	7.75	11.9
4-Hydroxy-3-methoxyphenylacetic acid (22)	7.9	6.54	6.43	9.14

weakly basic anion exchanger. All of the carboxylic acids were dissociated in water and therefore were held more strongly than in 1 mM hydrochloric acid. The tailing disappeared in 1 mM hydrochloric acid except for 2-hydroxybenzoic acid which was highly dissociated even in this medium. The large contributions of ion exchange to the retention of this acid are reflected in the high retention volume in weakly acid solution and in the large decrease in retention volume in 0.02 M HCl where only a small fraction of the acid was dissociated. The most striking effect is the large decrease caused by the presence of sodium chloride, which depresses sorption by ion exchange but, as already mentioned, results in a salting out of non-electrolytes. The observation that in 1 mM hydrochloric acid all of the weaker acids were held more strongly in the presence of sodium chloride shows that the salting-out effect on the undissociated acid had a much larger effect on D_v than the competing effect due to the decreased contributions from ion exchange. In the following discussion of the elution order of phenolic compounds and comparatively weak carboxylic acids in 1 mM hydrochloric acid the influence of ion exchange will therefore be disregarded.

Most of the chlorinated solutes were held so strongly in dilute acid that chromatographic separations were impractical. In order to depress the sorption, 3–7 M acetic acid was applied as eluent both with PVP and with the anion exchanger. The results given in Fig. 1 show that over the whole range the elution order of the chlorophenols was the same on both resins. The slope of the curves was higher for the

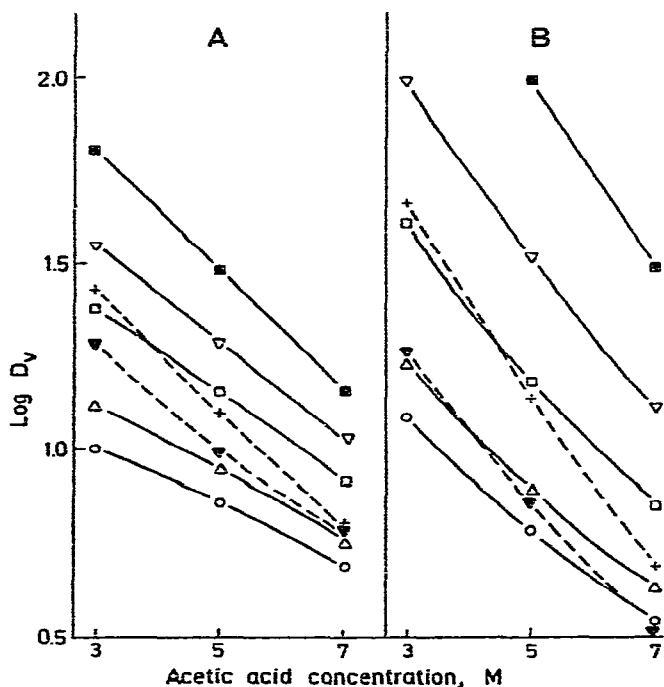


Fig. 1. The dependence of $\log D_v$ for chlorophenols on the acetic acid concentration. A = PVP, 30°; B = Dowex 1-X8, 70°. ○ = 2-Chlorophenol; ▽ = 2,4,5-trichlorophenol; △ = 3-chlorophenol; ■ = 2,3,4,5-tetrachlorophenol; + = 1-chloronaphthalene; ▼ = naphthalene; □ = 2,5-dichlorophenol.

tetrachlorophenol and trichlorophenol than for the dichlorophenol and monochlorophenol. The decreased sorption for these solutes can be ascribed to a blockage of proton-accepting sites in the resin phase by acetic acid, to the formation of association compounds with acetic acid and to the decreased contributions from non-polar interactions including those due to solute-water interactions (hydrophobic interactions). It is noteworthy that with both resins an extremely high slope was observed for 1-chloronaphthalene and that the curve intersected that of 2,5-dichlorophenol. Similarly, the effect of an increased eluent concentration was larger for naphthalene than for the chlorinated phenols having comparable D_v values. With the investigated solutes, the lowest slope was observed for benzene (not included in the figure) which exhibited the lowest D_v value among the solutes listed in Table III. The results with naphthalene and 1-chloronaphthalene reflect the very great effect of solute-solvent interactions in these systems. The results show that for separations of solutes of different types the choice of eluent concentration is more important than the choice between the anion exchanger and PVP.

The chromatogram given in Fig. 2 shows that 3 *M* acetic acid is a suitable medium for anion-exchange separation of compounds containing two aromatic nuclei. Seven added compounds were well separated from each other and from three unknown compounds which were present as impurities. Under the applied conditions, the retention time of the last compound was 3 h 50 min. For compounds held more strongly in this medium, a higher acetic acid concentration can be used to advantage. An example is illustrated in Fig. 3 where the separation of four chlorinated phenols in 7 *M* acetic acid required 60 min.

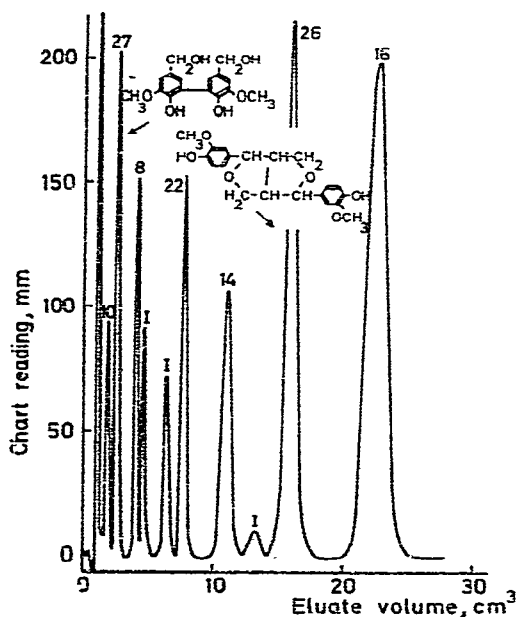


Fig. 2. Separation of seven aromatic compounds in 3 *M* acetic acid on Aminex A-28 (Ac^-) at 70°. Column, 350 × 1.9 mm. Nominal linear flow-rate, 3.8 cm/min. For compound numbers refer to Table II. Peaks denoted by I are due to impurities.

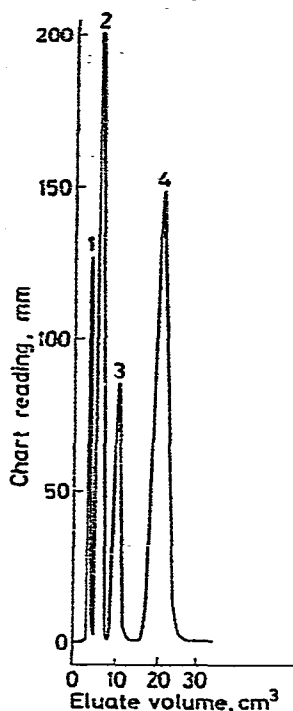


Fig. 3. Separation of (1) 3-chlorophenol, (2) 2,3-dichlorophenol, (3) 2,4,5-trichlorophenol and (4) 2,3,4,5-tetrachlorophenol in 7 *M* acetic acid on Aminex A-28 (Ac⁻) at 81°. Column, 160 × 3.0 mm. Nominal linear flow-rate, 5.9 cm/min.

Chromatograms illustrating the separation of benzene derivatives on PVP in 1 *mM* hydrochloric acid were presented previously¹. Equally good separations were obtained for most of the solutes containing two aromatic nuclei. Some of the studied solutes exhibited such high D_o values (Table II) that they could not be eluted in this medium within a reasonable time. Several compounds of this type were easily separated in acetic acid (Fig. 4). Unfortunately, the separation factors (α) for some solutes decrease markedly in acetic acid. Hence compounds 26 and 27 (Table II) which are well separated in 1 *mM* hydrochloric acid ($\alpha = 1.28$) cannot be easily resolved in 5 *M* acetic acid ($\alpha = 1.08$). On the other hand, these solutes can be most conveniently separated (Fig. 2) on an anion exchanger in 3 *M* acetic acid ($\alpha = 8.0$). Similarly, most of the chlorinated compounds could be separated in 5 *M* acetic acid. For some of the compounds, *e.g.*, 2,3-dichlorophenol and 2,5-dichlorophenol, the separation factor was unfavourable both on PVP and on the anion exchanger (Table III). These solutes were, however, well resolved by chromatography on a cation-exchange resin by elution with 1 *mM* hydrochloric acid⁷. For several of the other compounds listed in Tables II and III the separations were much better on the anion exchanger and on PVP than on the cation exchanger.

Relations between the structure of the non-electrolytes and their retention data

As a first approximation a swollen ion-exchange resin of the gel type can

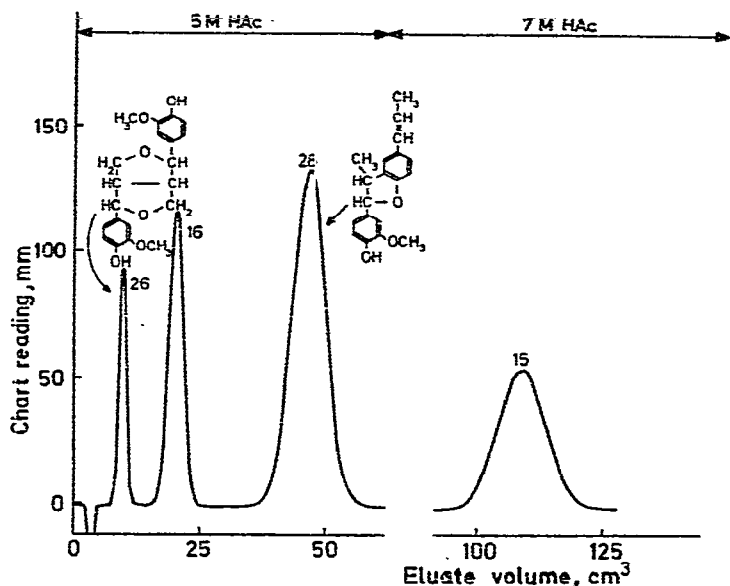


Fig. 4. Stepwise elution of four aromatic compounds in 5–7 *M* acetic acid on PVP at 30°. Column, 500 × 2.8 mm. Nominal linear flow-rate, 3.6 cm/min.

be considered as a concentrated homogeneous electrolyte solution. According to the Gibbs–Donnan theory, the distribution coefficient can be represented by the equation

$$\ln D_v = \ln(1 - \varepsilon_I) - \pi \bar{v} / RT - \ln(f_r / f)$$

where π is the swelling pressure, \bar{v} is the partial molar volume of the non-electrolyte and f_r/f is the ratio of its activity coefficients in the resin phase and in the external solution; R and T denote the gas constant and the thermodynamic temperature.

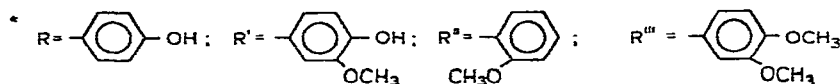
In dilute aqueous solutions the concentration of glycerol and other polyols in a swollen ion-exchange resin is lower than that in the external solution. This exclusion effect is mainly due to the pressure–volume term, while the activity-coefficient term is small⁸. Evidently the formation of hydrogen bonds between hydroxyl groups in aliphatic compounds and ion-exchange resins is of little importance in dilute aqueous solutions. The D_v value of glycerol (Table II) on the acetate form of an anion exchanger confirms this conclusion. The D_v value observed for PVP shows that the same conclusion is true for this polymer.

From previously published results, it is evident that on both types of resin the strong sorption of compounds like phenol (2) and 2-methoxyphenol (3) is mainly due to hydrogen bonding of the phenolic proton to proton-accepting groups in the resin and to non-polar interactions. Both types of interactions decrease the activity-coefficient ratio. Intramolecular hydrogen bonding explains the lower D_v value of 2-methoxyphenol on both resins. The introduction of a glycerol side chain (4) will increase the hydrogen bonding due to inductive effects, but, as shown in the table, the concentration of this compound inside the ion-exchange resin is lower than in the external solution ($D_v < 1 - \varepsilon_I$).

TABLE II

RETENTION DATA ON PVP IN 0.001 M HYDROCHLORIC ACID AT 30° AND ON AMINEX A-28 IN 3 M ACETIC ACID AT 70°

Compound*	PVP in HCl		Aminex in 3 M acetic acid		
	D_o	$\ln D_o$	D_o	$\ln D_o$	
1	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$	0.54	0.62	0.27	-1.31
2	RH	4.96	1.60	8.44	2.13
3	R'H	4.26	1.45	5.88	1.77
4	$\text{R}'\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$	1.21	0.19	0.5	-0.7
5	$\text{R}'\text{CH}_2\text{OH}$	3.22	1.17	1.81	0.59
6	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_3$	7.19	1.97	39.9	3.69
7	$\text{R}'\text{CH}_2\text{CH}=\text{CH}_2$	7.21	1.98	27.4	3.31
8	$\text{R}'\text{CH}=\text{CHCH}_2\text{OH}$	10.7	2.37	5.67	1.74
9	$\text{R}'\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	4.31	1.46	3.33	1.20
10	$\text{R}'\text{CH}(\text{OH})\text{CH}(\text{OH})\text{R}'$ CH_2OH	5.65	1.73	1.77	0.57
11	$\text{R}'\text{CH}(\text{OH})\text{CHR}'$ CH_2OH	5.69	1.74	1.65	0.50
12	$\text{R}'''\text{CH}(\text{OH})\text{CHOR}''$ CH_2OH	3.10	1.13	2.94	1.08
13	$\text{R}'\text{CH}(\text{OH})\text{CHOR}''$	5.81	1.76	3.38	1.22
14	$\text{R}'\text{CH}(\text{OH})\text{CH}_2\text{OR}''$	17.2	2.84	15.9	2.77
15	$\text{R}'\text{CH}=\text{CHR}'$	>65		>65	
16	$\text{R}'\text{COCH}_2\text{R}'$	>65		32.2	3.47
17	$\text{CH}_3\text{CH}_2\text{COOH}$	0.91	-0.094	1.63	0.49
18	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$	0.88	-0.13	2.57	0.94
19	$\text{CH}_2=\text{CHCOOH}$	1.18	0.17	3.01	1.10
20	$\text{CH}_3\text{CH}=\text{CHCOOH}$	1.27	0.24	2.95	1.08
21	RCH_2COOH	8.82	2.17	15.1	2.71
22	$\text{R}'\text{CH}_2\text{COOH}$	6.54	1.88	9.51	2.25
23	$\text{R}'\text{CH}_2\text{CH}_2\text{COOH}$	8.06	2.09	11.7	2.46
24	$\text{R}'\text{CH}=\text{CHCOOH}$	62	4.13	28.5	3.35
25	$\text{R}''\text{OCH}_2\text{COOH}$	>65		57	4.04
26	See fig. 2	26.7	3.28	23.5	3.16
27	See fig. 2	20.8	3.03	2.95	1.08
28	See fig. 4	>65		>65	



An approximate calculation⁹, based on the assumption that the swelling pressure of the anion exchanger is 20 MPa, shows that the increase in the partial molar volume by the introduction of a glycerol side chain in 2-methoxyphenol will lower $\ln D_o$ by only *ca.* 0.5, while the observed decrease was 2.47. This large change must therefore be due mainly to a dramatic decrease in non-polar interactions, due to the introduction of a strongly hydrophilic side chain. For PVP a similar but less dramatic change in D_o was observed. The results suggest that, under the applied

conditions, the contributions of hydrogen bonding relative to those of non-polar interactions are much larger for PVP than for the anion exchanger. We can therefore predict that a hydroxymethyl substituent in 2-methoxyphenol will depress the non-polar interactions. This will result in a decrease in $\ln D_e$ which will be less on both resins than that for a glycerol side chain and markedly higher for the anion exchanger than for PVP. The experiments (5) corroborated these predictions. Conversely, a propyl substituent (6) will increase the non-polar interactions. As expected, the increase in $\ln D_e$ was much larger on the anion exchanger than on PVP. An allyl substituent is less hydrophobic than a propyl group¹⁰. Increased non-polar interactions compared to 2-methoxyphenol seem to be mainly responsible for the increase in $\ln D_e$ for compound 7 on the anion exchanger. As expected, this increase was less than that for compound 6. The contributions from non-polar interactions will be less on PVP, while the contributions from enhanced hydrogen bonding will be more important on PVP. This explains the observation that the allyl substituent gave the same contribution to $\ln D_e$ as the more hydrophobic propyl substituent.

Inductive strengthening of hydrogen bonding will be an important factor when the double bond is conjugated with the aromatic ring. The large increase in $\ln D_e$ on PVP by the introduction of the rather hydrophilic $-\text{CH}=\text{CHCH}_2\text{OH}$ group (8) should therefore be mainly ascribed to larger contributions from hydrogen bonding. This factor will tend to increase the D_e value on the anion exchanger, but the effect will be less. The observation that the D_e value of compound 8 was slightly lower than that of 2-methoxyphenol must be ascribed to the effects of the pressure-volume term and to decreased non-polar interactions. For the corresponding saturated compound (9) it can be predicted that the contributions from hydrogen bonding should be much less. This was confirmed by the observation that its D_e value on PVP was much lower than that of the unsaturated compound (8). As expected the decrease in $\ln D_e$ compared to the unsaturated compound was less on the anion exchanger.

Naphthalene and two isomeric dihydroxynaphthalenes, which were the only polyaromatic compounds previously studied, exhibited very high D_e values on both resins. The results with compounds 10–13 show that the sorption was much less when two aromatic nuclei were separated by an aliphatic chain containing two hydroxyl groups. These results can be explained by the lower non-polar interactions due to the aliphatic hydroxyl groups. The effect of a glycol group (10) or a branched chain (11) was virtually the same. On PVP, compound 10, containing two 4-hydroxy-3-methoxyphenyl groups and two aliphatic hydroxyl groups, exhibited a D_e value which was almost twice that of compound 5, having only one 4-hydroxy-3-methoxyphenyl group and one aliphatic hydroxyl group. On the anion exchanger the D_e values were approximately the same for both compounds. The results confirm that the pressure-volume term cannot be neglected for large compounds with comparatively low non-polar interactions.

Compound 27 (Fig. 2), having one hydroxymethyl group linked to each of the aromatic rings, was held much more strongly on both resins than was its isomer (10). This result can be explained by the increased contributions from hydrogen bonding due to the directly bonded ring system. As expected, the increase in $\ln D_e$ was much larger on PVP than on the anion exchanger.

A comparison between compounds 13 and 14 shows that the elimination of one hydroxymethyl group in an aliphatic chain resulted in a large increase in $\ln D_e$.

on both resins. This effect, which can be ascribed to increased non-polar interactions, was, as expected, greater for the anion exchanger than for PVP.

Large non-polar interactions and strong hydrogen bonding explain the very high D_v value of compound 15 in which the aromatic rings are separated by a vinylene bridge. The non-polar interactions must be expected to be less for compound 16 which contains a carbonyl group. The fact that this compound was held more strongly on PVP than on the anion exchanger suggests larger contributions from hydrogen bonding on PVP. This is in agreement with previous results with 4-hydroxybenzaldehyde, which was held much more strongly than phenol on PVP¹ but less strongly than phenol on an anion exchanger in 3 *M* acetic acid⁴.

Previous studies of benzene derivatives showed that, for both types of resin, a phenolic hydroxyl group gave a larger contribution to D_v than a methoxyl group. The D_v values of compounds 12 and 13 show that the same conclusion is true for compounds of a more complex structure. The greater contributions of the phenolic hydroxyl group with PVP confirm that, under the applied conditions, hydrogen bonding has the greatest influence with PVP.

The acid eluents were chosen so that ion exchange had no effect on the sorption of the phenolic compounds. On the other hand, the carboxylic acids are dissociated to some extent in both of the acid media, which means that ion exchange is not eliminated completely. The low D_v values for the acyclic acids on PVP confirm that the ability of these acids to form hydrogen bonds with PVP in aqueous solution is small compared to that of benzoic acids. The unsaturated acids were retained more strongly than their saturated analogues, indicating a strengthening of the hydrogen bonding due to inductive effects. The fact that crotonic acid, the weaker acid, was held more strongly than acrylic acid indicates that non-polar interactions contribute to the sorption.

All of the acyclic acids (HA) were retained much more effectively by the anion exchanger in 3 *M* acetic acid than by PVP in 1 *mM* HCl. Their sorption is ascribed to the formation of counter ions of the type (HAAc⁻) in the resin phase¹¹. The observation that butanoic acid is held more strongly than propanoic acid confirms that non-polar interactions contribute to the sorption¹². The stability of the associated anions increases with increasing strength of the acid, and as expected the unsaturated acids are held more strongly than their saturated analogues. The elution order of crotonic and acrylic acids is in agreement with this pattern, although non-polar contributions will be more important for crotonic acid.

Ferulic acid (24) was held very strongly by both resins. It is noteworthy that the D_v values were much higher than those of the corresponding alcohol (8), indicating that hydrogen bonding between the carboxyl group and the proton-accepting resins contributed markedly to the sorption. This was confirmed by the high D_v value of compound 25 which contains a carboxylic acid group but lacks phenolic hydroxyl groups. It is seen that 25, the strongest acid among those listed in Table II, exhibited the highest D_v value on both resins. On both resins, dihydroferulic acid (23) exhibited a much lower D_v value than ferulic acid. The higher acid strength of the latter contributes to this effect, but no doubt the effect of the double bond (*cf.* compounds 8 and 9) is also of importance.

The strength of 4-hydroxyphenylacetic (21) and 4-hydroxy-3-methoxyphenylacetic acids (22) must be approximately the same. On both resins, compound 21 was

TABLE III

RETENTION DATA ON PVP IN 5 M ACETIC ACID AT 30° AND ON DOWEX 1-X8 IN 7 M ACETIC ACID AT 70°

Compound	PVP		Dowex 1-X8	
	D_e	$\ln D_e$	D_e	$\ln D_e$
Benzene	2.36	0.86	1.10	0.095
Chlorobenzene	3.43	1.23	1.56	0.45
Phenol	3.89	1.36	1.78	0.56
2-Chlorophenol	7.42	2.00	3.78	1.33
3-Chlorophenol	9.12	2.21	4.31	1.46
4-Chlorophenol	8.15	2.10	4.17	1.43
2,3-Dichlorophenol	15.4	2.73	7.01	1.95
2,4-Dichlorophenol	11.9	2.48	6.37	1.85
2,5-Dichlorophenol	14.7	2.69	7.03	1.95
2,6-Dichlorophenol	8.66	2.16	3.05	1.12
2,4,5-Trichlorophenol	19.7	2.98	12.9	2.56
2,4,6-Trichlorophenol	10.4	2.34	5.86	1.77
3,4,5-Trichlorophenol	24.0	3.18	14.9	2.70
2,3,4,5-Tetrachlorophenol	30.5	3.42	30.2	3.41
2,3,4,6-Tetrachlorophenol	16.6	2.81	17.1	2.84
2,3,5,6-Tetrachlorophenol	18.7	2.93	24.6	3.20
Pentachlorophenol	>50		>50	
3-Methylphenol	4.57	1.52	1.88	0.63
4-Chloro-3-methylphenol	9.45	2.25	3.99	1.38
Naphthalene	9.16	2.21	3.13	1.14
1-Chloronaphthalene	12.8	2.55	4.89	1.59
1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT)	>50		>50	

held more strongly than 22. This demonstrates that the carboxylic acid group and the phenolic group both contribute to hydrogen bonding with the resin. The lower D_e value of compound 22 is explained by intramolecular hydrogen bonding.

Chromatography on anion exchangers in methanol media shows that introduction of chloro groups into the aromatic rings leads to increased retention volumes¹³. The results given in Table III show that the same conclusion is true in aqueous media. With the hydrocarbons, this change can be related to increased non-polar interactions which are reflected in a decreased solubility in water. For phenolic compounds, increased contributions from hydrogen bonding with the resin are an additional factor.

As expected, 2-chlorophenol, which has the ability to form intramolecular hydrogen bonds, was held less strongly than its isomers. Likewise, 2,4,5-trichlorophenol had a lower D_e value than 3,4,5-trichlorophenol. The observation that 2,4,6-trichlorophenol and 2,6-dichlorophenol exhibited much lower D_e values than their isomers is explained by a combination of intramolecular hydrogen bonds and steric hindrance. For the same reason, the D_e values of the tetrachlorophenols with 2,6-substituents were much less than that of 2,3,4,5-tetrachlorophenol.

For compounds lacking intramolecular hydrogen bonds and steric hindrance, D_e should increase with increasing acid strength, providing that the effects of non-polar interactions are virtually the same. From experiments with cation-exchange resins⁷, we conclude that the non-polar interactions are almost the same for 4-chloro-

phenol ($pK_a = 9.37$, ref. 13) and 3-chlorophenol ($pK_a = 8.97$). As predicted, the stronger acid exhibited a higher D_r value on PVP and on the anion-exchange resin.

Even for compounds with intramolecular hydrogen bonds and steric hindrance, the stronger acids were held more firmly than comparable isomers. Hence, 2,3,5,6-tetrachlorophenol ($pK_a = 5.03$) and 2,3,4,6-tetrachlorophenol ($pK_a = 5.22$), which exhibited approximately the same D_r values on a cation exchanger, were eluted in the order of increasing acid strength both on PVP and on the anion exchanger. In agreement with this rule, 2,4-dichlorophenol, which is a weaker acid than 2,3-dichlorophenol and 2,5-dichlorophenol, exhibited the lowest D_r value.

The D_r value for 2,5-dichlorophenol ($pK_a = 7.51$) was the same as that of 2,3-dichlorophenol ($pK_a = 7.71$) on the anion exchanger. On PVP their order of elution was the reverse of that expected from the acid strength. These results may be explained by larger non-polar contributions, reflected in a much higher D_r value of 2,3-dichlorophenol on a cation exchanger.

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