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## CHROMATOGRAPHIC BEHAVIOUR OF AROMATIC COMPOUNDS ON ANION-EXCHANGE RESINS IN VARIOUS CARBOXYLATE FORMS

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### SUMMARY

Phenols, benzyl alcohols and aromatic carboxylate ions were chromatographed on an anion-exchange resin in aqueous acetate, glycolate, butyrate and tartrate solutions. Non-polar interactions of alkyl groups and hydrogen bonding between phenolic hydroxyl protons and the resin led to increased distribution coefficients of both ions and non-electrolytes, while internal hydrogen bonding between phenolic and vicinal methoxyl groups suppressed the hydrogen bonding with the resin. The distribution coefficients of most aromatic carboxylate ions were higher in 0.5 *M* than in 0.3 *M* sodium tartrate solution. A large increase in the activity coefficients of the aromatic ions in the eluent with increasing tartrate concentration explains this abnormal effect, which parallels the high salting out of aromatic non-electrolytes in tartrate compared to the other eluents.

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### INTRODUCTION

In anion exchange of strongly hydrophilic ions such as aldinate ions and oligomers built up from sugars and carboxylate anions the distribution coefficients decrease with increasing molecular volume<sup>1,2</sup>. Calculations based on the Gibbs-Donnan equation show that the pressure-volume term has a predominant influence on the equilibrium in systems of this type. Reversed affinity orders, *e.g.*, for the series  $\text{CH}_3(\text{CH}_2)_n\text{COO}^-$  and  $^-\text{OOC}(\text{CH}_2)_n\text{COO}^-$ , are explained by non-polar interactions which exert a larger effect than the pressure-volume term<sup>3,4</sup>. Little work has been devoted to studies of the ion-exchange affinity of aromatic carboxylate anions in aqueous solution, while the sorption of the undissociated acids has been studied by several investigators<sup>5</sup>. The main purpose of this investigation is to compare the effect of various substituents in aromatic carboxylate ions, and in other aromatic compounds, on the sorption onto anion-exchange resins in sodium salt solutions of aliphatic carboxylic acids.

## EXPERIMENTAL

Four batches containing equal amounts (by weight) of undried Dowex 1-X8 (10–17  $\mu\text{m}$ ) in the acetate form were slurried in water and transferred to four columns with an inner diameter of 2.4 mm. The exchange capacity was 0.99 mmol. This was determined in separate batches which were converted into the chloride form and washed with water. The chloride ions were eluted with sodium nitrate and determined potentiometrically.

One of the columns was conditioned by pumping 0.5 *M* sodium acetate solution through it for 1 h. The bed volume of the conditioned column was 0.75 ml. The other columns were converted into the glycolate, butyrate and tartrate forms by treatment with sodium salt solutions and conditioned in 0.5 *M* solution. The bed volume for the glycolate and butyrate columns was virtually the same as that obtained for the acetate resin, but was 5% lower for the tartrate form. This shrinkage was disregarded when calculating the distribution coefficients  $D_o$  from the relationship

$$D_o = \bar{v}/X - \varepsilon_1$$

where  $\bar{v}$  is the peak elution volume,  $X$  the column volume and  $\varepsilon_1$  ( $= 0.4$ ) the relative interstitial volume. The difference between  $\ln D_o$  for a parent compound, *e.g.*, phenol, and a substituted compound, *e.g.*, 4-methylphenol, in the same medium is denoted by  $\Delta$ .

The nominal linear (empty tube) flow-rate was 14.0  $\text{cm min}^{-1}$ . The aromatic compounds were dissolved in boiled distilled water. Sparingly soluble acids were added as their sodium salts. Single compounds were applied to the column and chromatographed to check the purity and determine the retention volume and response in the UV detector at 254 and 280 nm. The reported retention data were obtained with well separated mixtures of three to five compounds (2.0  $\mu\text{mol}$  per ml of each). In all the experiments the injected volume was 25  $\mu\text{l}$ .

The influence of the loaded amount of aromatic compounds was studied in 0.5 *M* sodium acetate at pH 7.0. For 2-methoxyphenol, which gave symmetric peaks, the elution volume was unaffected when the loaded amount was varied between 0.02 and 0.4  $\mu\text{mol}$ . Addition of benzyl alcohol, benzoic acid and 4-methoxybenzoic acid (0.1  $\mu\text{mol}$  of each) had no influence on the position of 2-methoxyphenol. For 4-hydroxy-3-methoxybenzaldehyde, which exhibited some tailing, an increased loading from 0.02  $\mu\text{mol}$  to 0.1  $\mu\text{mol}$  led to a decrease in the retention volume of 3%.

## RESULTS

*Influence of the eluent composition*

The eluents contained sodium salts of acetic, glycolic, *n*-butyric and L-tartaric acids and free acids so that the pH was 7.0. At this pH, variations of  $\pm 0.1$  pH unit had no detectable effect on the retention volumes for the aromatic carboxylate anions and for weakly acid solutes such as phenols and benzaldehyde, while the positions of 4-hydroxybenzaldehyde and hydroxymethoxybenzaldehydes, which are partially ionized under the applied conditions, were affected. At 60°C the  $D_o$  of 4-hydroxybenzaldehyde in 0.5 *M* sodium acetate was 56 at pH 6.0, 97 at pH 7.0 and 140 at

pH 8.0. Far-reaching conclusions cannot therefore be drawn from small differences in retention data of these compounds.

Table I shows that an increased sodium acetate concentration led to a large decrease in  $D_o$  for the hydroxybenzaldehydes, thus illustrating that ion exchange contributed markedly to the sorption of these solutes. Conversely, an increased eluent concentration resulted in an increased  $D_o$  value for unsubstituted benzaldehyde which is non-ionized at pH 7.

TABLE I

DISTRIBUTION COEFFICIENTS FOR BENZALDEHYDE AND DERIVATIVES AT pH 7.0 AND 60°C IN SOLUTIONS OF SODIUM SALTS

Substituents	Acetate		Glycolate	Butyrate	Tartrate
	0.5 M	1.0 M	0.5 M	0.5 M	0.5 M
None	7.1	7.9	7.1	6.4	12.6
4-Hydroxy	97	75	68	57	79
4-Hydroxy-3-methoxy	93	63	67	41	77
4-Hydroxy-3,5-dimethoxy	76	48	62	27	71

Similarly, salting out was observed for the phenols and benzyl alcohols. The increase in  $D_o$  was between 11 and 31% when 1 M instead of 0.5 M sodium acetate was used (Table II). For sodium tartrate the  $D_o$  increased by 17–41% when the tartrate concentration was raised from 0.3 to 0.5 mol l<sup>-1</sup>. In both acetate and tartrate the largest salting out effects were observed for the phenols with alkyl substituents while the lowest effects were found for 4-hydroxyphenol and 4-hydroxybenzyl alcohol.

To study further the salting out of non-ionized aromatic compounds the  $D_o$  was determined for benzyl alcohol, phenol and 4-methylphenol in acetate, glycolate, butyrate and tartrate solutions over a wider concentration range. In Fig. 1  $\ln D_o$  is plotted *versus* the molar eluent concentration ( $C$ ). It is seen that straight line relationships were obtained. Hence,  $\ln D_o - \ln D_o^0 = k_s C$  where the superscript 0 refers to the extrapolated value for pure water. The salting out parameter,  $k_s$ , differed somewhat for different compounds but no cross-over occurred. For all compounds the salting out parameters depended strongly on the medium. The slopes observed in sodium tartrate were much larger than those obtained in the other media. Even if the salting out parameters in tartrate are calculated from plots of  $\ln D_o$  *versus* moles of carboxylate per litre instead of molarity, the values are significantly higher than those in the other media. The smallest salting out parameters were obtained in sodium butyrate. Since butyrate anions are more hydrophobic than any of the other anions this result is consistent with the observation, discussed below, that hydrophobic interactions contribute markedly to the  $D_o$  values. As expected, larger salting out parameters were obtained in glycolate than in acetate.

According to the Gibbs–Donnan theory the molality in the resin phase ( $m_r$ ) divided by that in the external solution ( $m$ ) is determined by the equation

$$\ln m_r/m = -\pi \bar{v}/RT - \ln f_r/f$$

TABLE II  
RETENTION DATA FOR PHENOLS, BENZYL ALCOHOLS, BENZOATES AND PHENYLACETATES IN ACETATE, GLYCOLATE, BUTYRATE AND TARTRATE SOLUTIONS AT 60°C

Parent compounds and substituents	Acetate 0.5 M		Glycolate 0.5 M		Butyrate 0.5 M		Tartrate 0.3 M		Tartrate 0.5 M		Activity coefficient ratio	
	$D_o$	$\Delta$	$D_o$	$\Delta$	$D_o$	$\Delta$	$D_o$	$\Delta$	$D_o$	$\Delta$		
<i>Phenol</i>	29.2		21.3		29.4		30.9		39.3		1.22	1.27
4-Methyl	59	0.71	73	0.72	56	0.64	64	0.73	86	0.78	1.24	1.34
4-Ethyl	121	1.42	153	1.46	113	1.34	138	1.49	195	1.60	1.26	1.41
4- <i>n</i> -Propyl	260	2.2	340	2.3	210	2.1	320	2.3	450	2.4	1.31	1.41
4-Hydroxy	37.8	0.26	42.0	0.17	22.6	0.06	33.1	0.02	37.4	-0.05	1.11	1.19
4-Methoxy	34.7	0.17	40.5	0.13	25.6	0.18	28.1	0.25	50.0	0.24	1.17	1.26
2-Methoxy	20.1	-0.37	23.9	-0.39	17.3	-0.21	16.5	-0.58	25.6	-0.19	1.19	1.25
<i>Benzyl alcohol</i>	6.0		5.4		5.5		6.9		9.0		1.22	1.30
4-Hydroxy	12.5	0.73	14.6	0.69	9.3	0.53	10.3	0.63	12.1	0.56	1.17	1.17
4-Methoxy	8.1	0.30	10.1	0.32	7.7	0.35	6.4	0.15	10.9	0.46	1.25	1.29
4-Hydroxy-3-methoxy	8.3	0.32	10.0	0.31	7.2	0.29	6.7	0.20	9.8	0.35	1.20	1.20
<i>Benzoate</i>	64		70		31.3		31.2		32.7		1.15	1.35
4-Methyl	131	0.71	75	0.72	147	0.74	56	0.58	68	0.77	1.15	1.38
4-Ethyl	260	1.4	153	1.43	310	1.48	109	1.25	152	1.58	1.16	1.45
4- <i>n</i> -Propyl	590	2.2	350	2.3	700	2.30	230	2.0	380	2.5	1.19	1.46
4-Hydroxy	156	0.88	83	0.82	121	0.54	83	0.97	49.6	0.46	1.06	1.25
4-Methoxy	100	0.44	58	0.47	110	0.44	42.2	0.30	53	0.53	1.16	1.34
4-Hydroxy-3-methoxy	100	0.44	54	0.39	91	0.26	44.0	0.34	37.8	0.19	1.08	1.29
4-Hydroxy-3,5-dimethoxy	63	-0.02	36.3	-0.01	63	-0.12	23.2	-0.30	29.8	-0.05	1.15	1.38
<i>Phenylacetate</i>	40.0		44.8		19.4		20.6		21.5		1.09	1.35
4-Hydroxy	82	0.72	44.5	0.72	70	0.44	43.0	0.80	30.6	0.39	1.09	1.31
4-Methoxy	56	0.33	34.0	0.45	62	0.32	23.3	0.18	30.8	0.40	1.21	1.34
4-Hydroxy-3-methoxy	51	0.23	29.7	0.31	49.5	0.10	22.4	0.14	22.8	0.10	1.16	1.31
4-Hydroxy-3,5-dimethoxy	31.0	-0.25	18.7	-0.15	35.6	-0.23	11.4	-0.53	16.0	-0.25	1.21	1.41

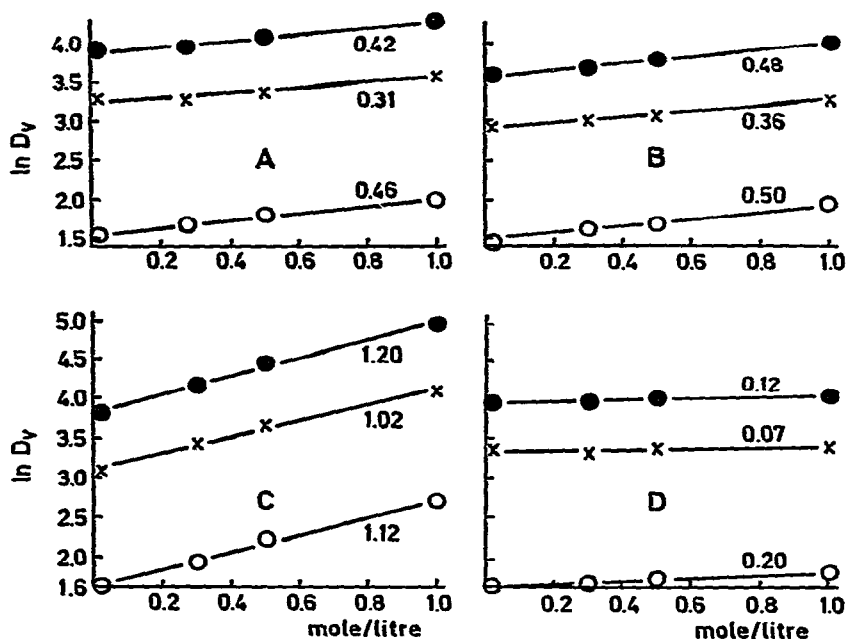


Fig. 1. Relationship between  $\ln D_v$  and eluent concentration in sodium acetate (A), sodium glycolate (B), sodium tartrate (C) and sodium butyrate (D) at 60°C. O, Benzyl alcohol; X, phenol; ●, 4-methylphenol. Values given on the lines refer to the salting out parameter  $k_s$  (slope of the straight lines calculated by the least-squares method).

where  $\pi$  is the swelling pressure,  $\bar{v}$  the partial molal volume of the solute and  $f_i/f^0$  the activity coefficient ratio<sup>6</sup>. A small increase in the eluent concentration will have a negligible influence on the swelling pressure and on the activity coefficients in the resin phase. As a good approximation,  $D_v$  is proportional to the molality ratio. This means that  $\ln D_v - \ln D_v^0 = \ln f/f^0$ . The ratio between the activity coefficients for the aromatic non-electrolyte at two concentrations of the eluent is therefore equal to the ratio between the distribution coefficients. The ratios  $f_{1.0}/f_{0.5}$  determined in sodium acetate and  $f_{0.5}/f_{0.3}$  determined in sodium tartrate are listed in Table II. Since the concentration of the non-electrolyte is low,  $f^0$  can be taken as unity. Hence,  $\ln f = k_s C$ .

In agreement with the Gibbs-Donnan theory the  $D_v$  values for the carboxylate anions decreased markedly when the acetate concentration (pH 7.0) was increased from 0.5 to 1.0 mol l<sup>-1</sup> (Table II). The decrease varied between 39% (4-methoxyphenylacetate) and 47% (4-hydroxybenzoate). Hence, it was significantly less than the value (50%) calculated for the exchange of ions of equal charge under the idealized conditions that the activity coefficient term, the swelling pressure and the concentration of eluting anions (in this case acetate) in the resin phase are unaffected by an increase in eluent concentration by a factor of 2. The individual differences for different aromatic ions show that specific interactions reflected in the activity coefficients are affected by the eluent concentration.

Under the same idealized conditions the calculated  $D_v$  values for the carboxylate anions in 0.5 M tartrate should be 23% lower than those in 0.3 M tartrate

solution. As shown in Table II a decrease of 3% was observed for 4-hydroxybenzoate ions while increased  $D_o$  values were obtained for the other ionic species investigated. The largest increase was obtained for 4-ethylbenzoate and 4-*n*-propylbenzoate (13%). Evidently, large interactions reflected in the activity coefficients must be responsible for the anomalous elution behaviour of the aromatic carboxylate anions in tartrate solution.

To elucidate further the abnormal elution behaviour in tartrate solutions, the  $D_o$  values for chloride ions were determined at various tartrate concentrations. When the concentration was changed from 0.3 to 0.5 mol l<sup>-1</sup> the  $D_o$  decreased from 5.77 to 4.82 which corresponds to 16% while, as already mentioned, the decrease calculated for idealized conditions is 23%. In 0.1 *M* tartrate solution the  $D_o$  was 8.33 compared to 5.77 (0.3/0.1)<sup>0.5</sup> = 9.99 calculated under idealized conditions from the value recorded in 0.3 *M* tartrate solution. The results show that the activity coefficient term cannot be disregarded even for the chloride-tartrate system, but that the deviations are much smaller than those observed for the aromatic carboxylate anions.

The aromatic carboxylate ions (A) were held so strongly in 0.02–0.10 *M* sodium acetate solutions, which are suitable eluents for strongly hydrophilic aliphatic carboxylate ions<sup>2</sup>, that the  $D_o$  values could not be accurately determined. Accordingly, the calculated pressure-volume term in the Gibbs-Donnan equation was smaller than the activity coefficient term indicating that specific interactions were of great importance for the aromatic anions.

$$\ln \frac{[A]_r}{[A]} \cdot \frac{[B]}{[B]_r} = \pi(\bar{v}_B - \bar{v}_A)/RT + \ln f_{B_r} \cdot f_A/f_{A_r} \cdot f_B \quad (= \ln k)$$

$D_o$  is proportional to  $[A]_r/[A]$ . A is present in trace amounts. The activity coefficients in the resin phase are therefore determined by the concentration of the eluent anion,  $[B]_r$ . If the effect of the eluent concentration,  $[NaB]$ , on the swelling pressure and the electrolyte invasion can be disregarded, we obtain

$$\frac{D_o'}{D_o} \cdot \frac{[B]'}{[B]_r} = \frac{f_A' \cdot f_B'}{f_B \cdot f_A}$$

where the superscripts refer to two different concentrations of the eluent.

For sodium acetate<sup>7</sup> the activity coefficient in 1 *M* solution is virtually the same as in 0.5 *M* solution. This means that the ratio between the activity coefficients of the aromatic anion in 1 *M* sodium acetate ( $f_{1.0}$ ) to that in 0.5 *M* sodium acetate ( $f_{0.5}$ ) is equal to the ratio between the distribution coefficients multiplied by 2. This ratio has been calculated for all aromatic anions studied. With the same approximations the ratio between the activity coefficient of the aromatic anions in 0.5 *M* sodium tartrate ( $f_{0.5}$ ) to that in 0.3 *M* sodium tartrate is obtained from the ratio between the  $D_o$  values multiplied by 1.29. The results are given in Table II.

It is noteworthy that for all non-electrolytes the ratio  $f_{1.0}/f_{0.5}$  in sodium acetate was lower than or equal to the ratio  $f_{0.5}/f_{0.3}$  in sodium tartrate. This result shows that for all non-electrolytes the salting out was much more effective in sodium tartrate than in sodium acetate. In both media the lowest ratio was observed for the most hydrophilic species (4-hydroxyphenol and 4-hydroxybenzyl alcohol) while alkylphenols exhibited larger values.

For all benzoates and phenylacetates the ratio  $f_{1.0}/f_{0.5}$  in sodium acetate was much lower than the ratio  $f_{0.5}/f_{0.3}$  in sodium tartrate. In both media 4-hydroxybenzoate exhibited the lowest ratio among the benzoate anions, while the less hydrophilic species (alkylbenzoates and 4-hydroxy-3,5-dimethoxybenzoate) exhibited high values. Similarly, 4-hydroxyphenylacetate exhibited a lower ratio than 4-hydroxy-3,5-dimethoxyphenylacetate both in acetate and in tartrate.

The results show that the effect of an increase in eluent concentrations on the activity coefficients of the aromatic carboxylate anions in the eluent parallels the effect of an increased concentration on the activity coefficients of non-electrolytes of similar structure. In addition, the type of anion in the eluent has a similar influence on the activity coefficients in the external solution of both aromatic anions and uncharged aromatic compounds. Hence, interactions in the external solution in which the eluting anions are involved and which greatly affect the activity coefficients of the aromatic anions are of the same kind as the interactions which determine the salting out of the uncharged aromatic solutes. It should therefore be possible to predict the elution behaviour of an eluent during the elution of aromatic anions from salting out experiments with related non-electrolytes. As shown above (Fig. 1) sodium butyrate gave much smaller salting out effects for non-electrolytes than sodium acetate and sodium tartrate. Hence, it can be predicted that in butyrate solution the activity coefficient ratios for aromatic anions should be lower, and more close to unity, than the corresponding values determined for acetate and tartrate. This was confirmed by the results given in Table III. It is noteworthy that in butyrate, as in acetate and tartrate, the anions with 4-hydroxy-3-methoxy substituents exhibited lower activity coefficient ratios than the more hydrophobic anions with 4-hydroxy-3,5-dimethoxy substituents.

TABLE III

VOLUME DISTRIBUTION COEFFICIENT ( $D_v$ ) FOR AROMATIC CARBOXYLATE ANIONS IN 0.3 M, 0.5 M AND 1.0 M SODIUM BUTYRATE AND THE RATIO BETWEEN THE ACTIVITY COEFFICIENTS ( $f$ ) OF THE AROMATIC ANIONS IN THESE MEDIA AT 60°C

The activity coefficients for sodium butyrate at 25°C reported by Harned and Owen<sup>7</sup> were used in these calculations. If these activity coefficients are disregarded,  $f_{0.5}/f_{0.3}$  decrease by 1% and  $f_{1.0}/f_{0.5}$  by ca. 10%

Anion	Distribution coefficients			$f_{0.5}/f_{0.3}$	$f_{1.0}/f_{0.5}$
	0.3 M	0.5 M	1.0 M		
4-Methylbenzoate	88	56	26.8	1.08	1.06
4-Hydroxy-3-methoxybenzoate	79	44	19.1	0.94	0.96
4-Hydroxy-3,5-dimethoxybenzoate	37.1	23.2	10.6	1.06	1.01
4-Hydroxy-3-methoxyphenylacetate	40.1	22.4	10.4	0.94	1.03
3-Hydroxy-3,5-dimethoxyphenylacetate	17.4	11.4	5.5	1.11	1.07

#### *Influence of substituents on the retention data*

The sorption of aromatic non-electrolytes from aqueous solution onto different adsorbents, including anion-exchange resins, is markedly higher for solutes containing non-polar substituents than for the parent compound<sup>5,8</sup>. The elution order phenol < 4-methylphenol < 4-ethylphenol < 4-*n*-propylphenol (Table II) obtained in-

dependent of the ionic form of the anion exchanger shows that non-polar interactions including hydrophobic interactions (sorption enforced by water-structure<sup>3</sup>) contribute markedly to the observed distribution coefficients.

Enhanced non-polar interactions must also be responsible for the higher  $D_o$  of 4-alkylbenzoates compared to benzoate. In all media the  $\Delta$  values for all alkylbenzoates were virtually the same as obtained for the corresponding 4-alkylphenols in the same medium. It should be recalled that under the applied conditions the phenols were non-dissociated while the aromatic carboxylic acids were almost 100% dissociated. Despite this difference the incremental change (decrease) in free energy for the transfer from the eluent to resin phase, resulting from the introduction of an alkyl group, was virtually the same for the non-electrolyte as for the ion. The results confirm that hydrophobic substituents have a marked influence on the ion-exchange equilibrium and show that under favourable conditions this effect can be predicted from independent data. For both phenols and benzoates the highest  $\Delta$  values resulting from the introduction of the alkyl groups were found for 0.5  $M$  tartrate solution, while the lowest values were observed in butyrate solution. An increase in  $\Delta$  with increasing eluent concentration can be traced in sodium acetate solution for both phenols and benzoates. This concentration effect was larger in tartrate medium. The results are consistent with the observation that hydrophobic species are salted out more effectively by tartrate than by the other eluents.

Methoxyl groups are less hydrophobic than methyl groups. Accordingly, methoxyl groups in *para* positions in phenol, benzoate and phenylacetate led to a smaller increase in  $\ln D_o$  than that observed for methyl groups. Again, the largest effect in 0.5  $M$  solutions was obtained for the tartrate form and the smallest effect for the butyrate form. In butyrate medium the  $D_o$  for 4-methoxyphenol was slightly lower than that of phenol. The observation that  $\Delta$  depends strongly on the parent compound indicates that the methoxyl group affects other factors of importance for the sorption than the non-polar interactions. Hence, 4-methoxyphenol is a weaker acid than phenol which means that the methoxyl group will decrease the hydrogen bonding between the phenolic hydroxyl group and the resin. Similarly, the substituent weakens the strength of benzoic acid which may affect the ion-exchange affinity of the 4-methoxybenzoate ion<sup>3</sup>.

Hydrophilic substituents suppress the non-polar interactions and, provided that other effects are small, their introduction will lead to decreasing  $D_o$  values. Hence, the introduction of phenolic hydroxyl groups in uncharged aromatic compounds leads to a decreased sorption from aqueous solution<sup>8</sup> onto non-ionic styrene-divinylbenzene resins. For anion-exchange resins in the acetate form<sup>5</sup>, and for other adsorbents<sup>9</sup> containing groups with a strong ability to participate in hydrogen bonding by serving as proton acceptors, hydrogen bonding with the adsorbent gives a positive contribution to  $\ln D_o$  which can be larger than the decrease due to the lower hydrophobic interactions.

Table II shows that a phenolic hydroxyl group in the *para* position in benzoate and phenylacetate resulted in markedly increased distribution coefficients, indicating that hydrogen bonding between the phenolic proton and the resin contributes markedly to the ion-exchange affinity. The  $\Delta$  values were lower in tartrate and higher in butyrate than in the other media. These values differed somewhat for the two types of aromatic anions. We conclude that the suppression of the non-polar interactions



had less effect on  $D_o$  than the hydrogen bonding with the resin and that the non-polar interactions have a greater influence on the equilibrium in tartrate medium than in butyrate.

In all media the effect of a second hydroxyl group in the *para* position in phenol was much less, and in 0.5 *M* tartrate  $\Delta$  was slightly negative. The results indicate that hydrogen bonding between phenols serving as hydrogen donors and the resin contributes to the sorption not only on acetate resins but also on the other ionic forms, and that the medium has a great influence on the effect of a second hydroxyl group. The acid strength of 1,4-dihydroxybenzene is lower than that of phenol. Hence, hydrogen bonding between the first hydroxyl group and the resin is less favoured than for phenol. This can explain the comparatively low  $\Delta$  values.

In agreement with previous investigations<sup>5</sup> under other conditions, 2-methoxyphenol was retained less strongly than phenol by the acetate resin. This is ascribed to intramolecular hydrogen bonding which weakens the hydrogen bonding to the resin. As shown in Table II, negative  $\Delta$  values were also observed with the other resin forms. Similarly, 4-hydroxy-3-methoxybenzaldehyde and 4-hydroxy-3-methoxybenzyl alcohol were, in all media, held less strongly than the corresponding compounds lacking the methoxyl group. If hydrogen bonding between the phenolic hydroxyl group and a vicinal methoxyl group is also important for the retention of carboxylate anions, it can be predicted that 4-hydroxy-3-methoxybenzoate and 4-hydroxy-3-methoxyphenylacetate should exhibit lower  $D_o$  values than the corresponding anions without the methoxyl group. Table II shows that this holds true. Both for phenol and for the carboxylate anions the smallest effect of the methoxyl group on  $\ln D_o$  was found in tartrate medium, while the largest effect was obtained in butyrate. A rough estimate of  $\ln D_o$  for the substituted anions can be obtained by adding  $\Delta$  for 2-methoxyphenol to  $\ln D_o$  of the 4-hydroxy substituted anions. In all media the calculated values were slightly higher than the observed values. The results permit the conclusion that internal hydrogen bonding between phenolic hydroxyl groups and a vicinal methoxyl group leads to lowered  $D_o$  values of both non-ionized and ionized aromatic species.

In agreement with this conclusion, 4-hydroxy-3,5-dimethoxybenzoate and 4-hydroxy-3,5-dimethoxyphenylacetate exhibited lower  $D_o$  values than the corresponding anions with one methoxyl group. Again, the smallest effect of the second methoxyl group was obtained with the tartrate resin while the largest effect was found with the butyrate resin. The large decrease in  $\ln D_o$  resulting from the second methoxyl group indicates that, in addition to a strengthened internal hydrogen bonding, the second methoxyl group leads to a steric shielding which will further suppress hydrogen bonding between the phenolic hydrogen in the aromatic anions and the resin. Effective internal hydrogen bonding and steric shielding can also explain the lower  $D_o$  of 4-hydroxy-3,5-dimethoxybenzaldehyde compared to 4-hydroxy-3-methoxybenzaldehyde.

#### *Influence of the ionic form*

The larger activity coefficients of the non-electrolytes in glycolate than in butyrate solutions (Fig. 1) shows that glycolate anions in the external solution have a greater ability than butyrate anions to push the aromatic solutes into the resin phase. It is therefore reasonable to assume that, at zero concentration in the external solution, glycolate ions in the resin would tend to push the solutes into the external

solution more effectively than the butyrate counter ions. This offers an explanation for the higher  $D_o^0$  values observed for butyrate than for glycolate (Fig. 1). As expected, acetate takes an intermediate position. The results lend additional support to the conclusion that hydrophobic interactions contribute to the distribution coefficients for the non-electrolytes. It is noteworthy that the structure of the carboxylate counter ions has a modest influence on  $D_o^0$ . The observation that higher values were obtained for the tartrate resin than for the glycolate resin can be related to the lower swelling pressure for the resin containing divalent anions.

The selectivity coefficient  $k_{B/Cl}$  for the ion-exchange equilibrium between butyrate and chloride ions on Dowex 1-X10 was found to be approximately 0.24 for resins with the exchange groups 50–95% occupied by chloride ions<sup>3</sup>. For the exchange between acetate and chloride the corresponding value was approximately 0.12. The higher value for butyrate is explained by larger non-polar interactions. If the selectivity coefficients were independent of the relative amounts of ions in the resins the ratio between the  $D_o$  of the aromatic carboxylate anions in 0.5 *M* butyrate and their  $D_o$  in 0.5 *M* acetate should be approximately 0.5. The observed values varied between 0.37 and 0.53. The highest values were obtained for 4-hydroxybenzoate and 4-hydroxyphenylacetate, while the lowest values were recorded for benzoate and phenylacetate with 4-hydroxy-3,5-methoxy substituents. It is noteworthy that both for the unsubstituted anions and for the derivatives virtually the same ratio was found for benzoates and phenylacetates.

No relevant data which permit a prediction of the ratio between  $D_o$  in glycolate to that in acetate seem to be available. The observed ratio varied between 0.78 and 1.19. The lowest ratio was observed for the carboxylate ions with a phenolic hydroxyl group in the *para* position. In contrast to the ratio between  $D_o$  in butyrate and acetate, this ratio depended on the parent compound. For all investigated species a higher ratio was found for phenylacetates than for benzoates. The results indicate that interactions in which the hydroxyl group in the glycolate ions are involved exert a great influence on the ion-exchange equilibrium.

#### *Influence of the temperature*

The elution of benzaldehyde, 4-hydroxy-3-methoxybenzaldehyde and the three aromatic anions listed in Table IV was studied in 0.5 *M* solutions of sodium acetate, glycolate, butyrate and tartrate at 15, 30, 45 and 60°C. The distribution coefficients decreased markedly with increasing temperature. Plots of  $\ln D_o$  versus  $1/T$  gave straight lines for all investigated systems. Hence, the enthalpy change was independent of the temperature. The slope showed that the sorption was strongly exothermic. For reasons already mentioned, the results with the substituted benzaldehyde will not be discussed further. The results obtained with the other solutes are given in Fig. 2 and Table IV. The lowest numerical enthalpy values were, in all media, obtained for benzaldehyde and the highest values for 4-hydroxy-3-methoxybenzoate which was also held more strongly by all ionic forms of the resin than the other aromatic carboxylate ions investigated.

As already mentioned, the activity coefficients for the aromatic anions in the external solution depended on the eluent concentration. Any generally valid comparisons between the changes in free energy and entropy cannot therefore be based upon available data. The calculations of these thermodynamic functions have there-

TABLE IV  
THERMODYNAMIC FUNCTIONS OF ANION-EXCHANGE EQUILIBRIA AT 30°C

Aromatic anions and eluents	$-\Delta\bar{H}$ (kJ mol <sup>-1</sup> )	$-\Delta\bar{G}$ (kJ mol <sup>-1</sup> )	$-\Delta\bar{S}$ (J mol <sup>-1</sup> /K <sup>-1</sup> )
<i>4-Hydroxy-3,5-dimethoxyphenylacetate</i>			
0.5 M Sodium acetate	11.9	7.28	15.3
0.5 M Sodium glycolate	12.1	7.68	14.4
0.5 M Sodium butyrate	12.4	4.76	25.3
<i>4-Hydroxy-3-methoxyphenylacetate</i>			
0.5 M Sodium acetate	12.7	8.54	13.6
0.5 M Sodium glycolate	12.3	8.54	12.3
0.5 M Sodium butyrate	13.4	6.70	22.0
<i>4-Hydroxy-3-methoxybenzoate</i>			
0.5 M Sodium acetate	14.6	10.43	13.7
0.5 M Sodium glycolate	14.5	10.23	13.9
0.5 M Sodium butyrate	15.8	8.44	24.1

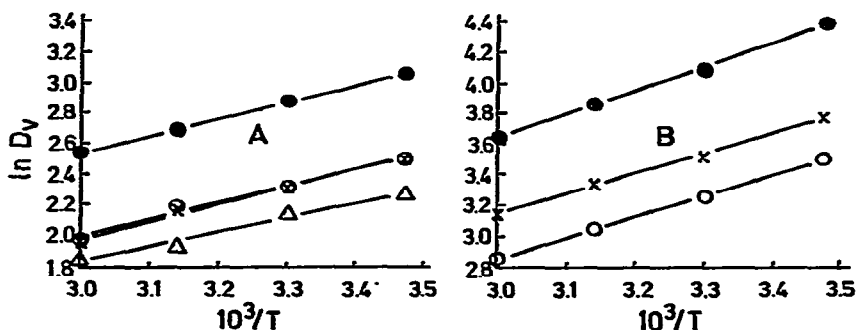


Fig. 2. Dependence of  $\ln D_v$  on  $1/T$ . A, Benzaldehyde in 0.5 M solutions of: tartrate (●),  $\Delta H = -9.48$ ; acetate (X),  $\Delta H = -9.34$ ; glycolate (○),  $\Delta H = -9.08$ ; butyrate (△),  $\Delta H = -7.64$ . B, Various anions in 0.5 M sodium tartrate: 4-hydroxy-3-methoxybenzoate (●),  $\Delta H = -12.8$ ; 4-hydroxy-3-methoxyphenylacetate (X),  $\Delta H = -11.0$ ; 4-hydroxy-3,5-dimethoxyphenylacetate (○),  $\Delta H = -11.3$ . The change in enthalpy,  $\Delta H$ , is in kJ mol<sup>-1</sup>.

fore been restricted to the ion-exchange equilibria in 0.5 M solutions of the singly charged eluents. The apparent enthalpy change,  $\Delta\bar{H}$ , was calculated by the least-squares method from the straight line relationship between  $\ln D_v$  (or  $\ln k$ ) and  $1/T$ . The  $\Delta\bar{H}$  value refers to the transfer of the ions from, and into, the applied eluents. The corresponding changes in free energy ( $\Delta\bar{G}$ ) and entropy ( $\Delta\bar{S}$ ) were calculated from the equations:

$$\Delta\bar{G} = -RT \ln k$$

$$\Delta\bar{S} = (\Delta\bar{H} - \Delta\bar{G})/T$$

The results showed that, as for  $\Delta\bar{H}$ , the  $\Delta\bar{S}$  values were virtually independent of the temperature, and therefore only the values obtained at 30°C are given in Table IV.

Table IV shows that the influence of the eluent anions on  $\Delta\bar{H}$  was rather small for the studied aromatic anions. This may indicate that exothermic interactions (e.g., hydrogen bonding with the resin) and endothermic interactions (e.g., breakage of internal hydrogen bonds) were affected to a modest extent by the structural differences in the eluting anions. The change in entropy was negative in all systems. For acetate and glycolate solutions —  $\Delta\bar{H}$  had a much larger influence on the change in free energy than the entropy term. The entropy change calculated for the acetate and glycolate systems differed only slightly, while  $\Delta\bar{S}$  was more negative for the exchanges in butyrate. A possible explanation is that hydrophobic (water-structure enforced) effects which contribute to an increased  $\Delta\bar{S}$  are more important in the less hydrophobic acetate and glycolate systems than in the butyrate systems. The results are consistent with the observation, mentioned above, that the contribution to  $\ln D_v$  resulting from the introduction of an alkyl or methoxyl group in phenols and carboxylate anions is less or more negative in butyrate medium than in any of the other media under investigation.

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#### REFERENCES

- 1 O. Samuelson and L. O. Wallenius, *J. Chromatogr.*, **12** (1963) 236.
- 2 O. Samuelson, *Advan. Chromatogr.*, **16** (1978) 113.
- 3 B. Chu, D. C. Whitney and R. M. Diamond, *J. Inorg. Nucl. Chem.*, **24** (1962) 1405.
- 4 L. Bengtsson and O. Samuelson, *J. Chromatogr.*, **61** (1971) 101.
- 5 L. M. Jahangir, L. Olsson and O. Samuelson, *Talanta*, **22** (1975) 973.
- 6 M. Mattisson and O. Samuelson, *Acta Chem. Scand.*, **12** (1958) 1386.
- 7 H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1958.
- 8 L. M. Jahangir and O. Samuelson, *Anal. Chim. Acta*, **85** (1976) 103.
- 9 L. Olsson and O. Samuelson, *J. Chromatogr.*, **93** (1974) 189.