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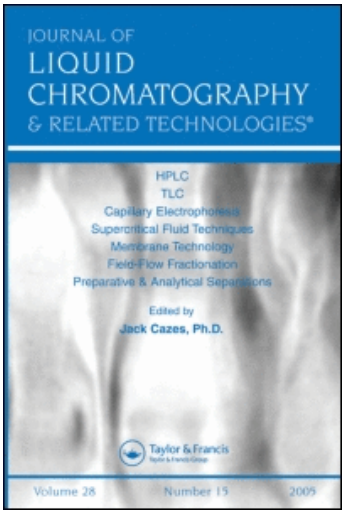


**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
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# The Chromatographic Behavior of some Hydrophilic Dyes and Dye Intermediates on Thin Layers of Strong and Weak Ion Exchangers

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**To cite this Article** Freeman, H. S. , Hao, Z. and Hsu, W. -N.(1989) 'The Chromatographic Behavior of some Hydrophilic Dyes and Dye Intermediates on Thin Layers of Strong and Weak Ion Exchangers', Journal of Liquid Chromatography & Related Technologies, 12: 6, 919 — 935
**To link to this Article: DOI:** 10.1080/01483918908051770
**URL:** http://dx.doi.org/10.1080/01483918908051770

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JOURNAL OF LIQUID CHROMATOGRAPHY, 12(6), 919-935 (1989)

# THE CHROMATOGRAPHIC BEHAVIOR OF SOME HYDROPHILIC DYES AND DYE INTERMEDIATES ON THIN LAYERS OF STRONG AND WEAK ION EXCHANGERS

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**ABSTRACT**

The chromatographic behavior of some polar organic dyes and dye intermediates on thin layers of various forms of cationic and anionic exchange resins has been investigated. The results of this study indicate that the stationary ion and the mobile ion of both types of exchangers greatly affect both the level of tailing and the $R_f$ values of the adsorbed compounds. It is also clear from this study that these resins are more suitable for evaluating the relatively simple dyes containing an $SO_3Na$ group than the higher molecular weight polyazo direct dyes used on cellulosic substrates, and that the $Li^+$ and $H^+$ forms of the cation exchangers work better than their counterparts. On the other hand, cationic dye molecules require the use of anion exchangers, with the -OAc form giving better chromatograms than the $ClO_4^-$ form.

## INTRODUCTION

In previous papers from these laboratories, we reported the results of our work involving the evaluation of dry column



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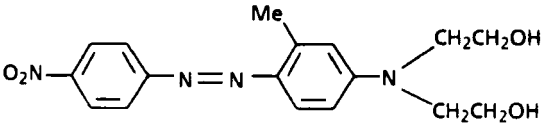


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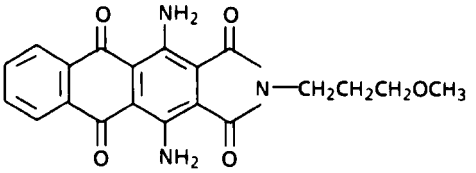


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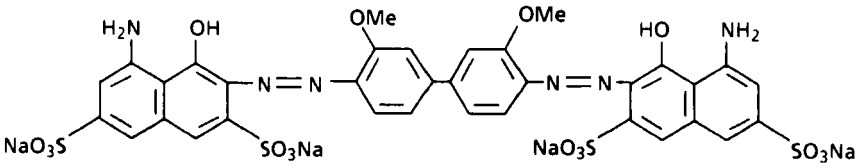


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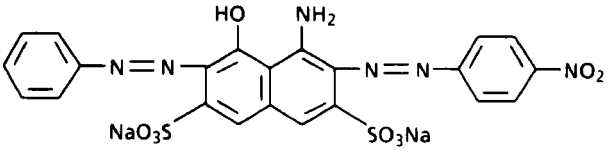


4. Acid Black 1

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chromatography (1), countercurrent chromatography (2,3), and analytical HPLC (4) as procedures for the generation of useful quantities of synthetic dyes in a form that is suitable for toxicological testing. Each of these procedures proved quite satisfactory for the purification of relatively hydrophobic dyes such as **1** and **2**, but much less so for the removal of the impurities in large hydrophilic dyes like **3** and **4**.

Our more recent work in this area has included the evaluation of ion exchange resins as substrates for the purification of hydrophilic dyes. The first step in this effort was the development of useful solvent systems and the identification of suitable resins. To meet this initial objective, some commercially available ion exchange TLC plates were obtained and used much in the same way as reported in papers describing (5-7) other ionic compounds.

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The commercial resins used were thin layers (0.10-0.12 mM) of ion exchangers in which the resins are bound to plastic sheets (chromatosheets) of poly(ethylene terephthalate). In one commercial exchanger (Fixion 50x8, 2x8), silica gel is used as the principle substrate of the fixing compound. The matrix used is polystyrol containing 8% divinylbenzene. The cation exchanger (Fixion 50x8) contains $SO_3Na$ groups in the sodium salt form, and the anion exchanger (Fixion 2x8) contains dimethylhydroxyethyl ammonium groups with acetate counter ions. It is believed (8) that the $SO_3Na$ and the $^-OAc$ containing resins correspond to the resins Dowex 50x8 and Dowex 2x8, respectively. In the second product the cation exchanger is a coating of Cellulose 300 di-

ethylaminoethyl tertiary amine (CEL 300 DEAE), and the anion exchanger is a coating of Cellulose 300 carboxymethyl (CEL 300 CM).

## EXPERIMENTAL

### Procedure for Equilibrating and Changing the Ionic Form of the Resins

The Fixion chromatosheet was placed on a clean, dry glass plate (20cm by 20cm) with the resin coating facing outward. A piece of filter paper (15cm by 20cm) was placed along the upper edge of the chromatosheet such that the filter paper covered the uppermost 1cm portion of the sheet. The paper was used to assist in the evaporation of the solvent during conditioning, and was held in place by a thin glass rod which was in turn held by a clothespin.

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To equilibrate the chromatosheet for use with a buffer, a 30-fold dilution of the buffer was allowed to continuously migrate up the plate for 24h. In some instances the adsorbent affixed to the immersed part of plate separated from the plate by the end of the equilibration. This problem was minimized by using a 1cm liquid level, and by removing a 1cm band of resin from the bottom of the plate. The plates were allowed to dry, and were labeled and stored in a TLC plate chamber at room temperature.

### Preparation of the Acid ($H^+$), $NH_4^+$, and $Li^+$ Forms of the Cation Exchangers

The commercial form ($Na^+$) of the exchanger was placed in a tank containing a 1cm deep 1M solution of HCl, LiBr, or $NH_4Cl$.

The plate was allowed to develop for 24h and to dry overnight at room temperature.

Preparation of the $ClO_4^-$ Form of the Anion Exchangers

The commercial form ($OAc^-$) of anion exchanger was placed in tank containing 1M sodium perchlorate (1cm deep). The plate was allowed to develop for 24h and to dry overnight at room temperature.

Experimental Conditions for Plate Development

The chromatosheet which had previously been converted to the desired ionic form, or to be used in the ionic form supplied by the manufacturer, was marked using a soft black pencil with the appropriate symbols, solvent systems, and starting line. A convenient starting line was located 3cm from the bottom of the sheet. From both sides of the sheet, left and right vertically, a 1mm wide stripe of resin layer was removed in order to promote even development. The plate development was performed in conventional chromatography tanks.

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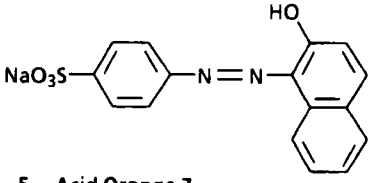
An example of a typical separation is outlined for Acid Red 52 (**7**). A 1% solution of **7** was spotted onto the $H^+$ form of a 4cm x 8.5cm Fixion 50x8 plate. The chromatosheet was dried using a hot air gun and developed in EtOH:$H_2O$/1:1. The solvent was allowed to travel a distance of 6cm on the chromatosheet. The solvent front was then marked and the plate was allowed to air dry.

## RESULTS AND DISCUSSION

Figures 1 and 2 contain the structures of the dyes and dye intermediates used in this investigation. A solution of each



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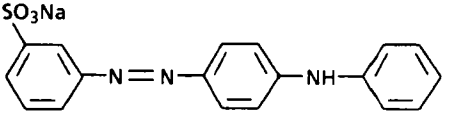

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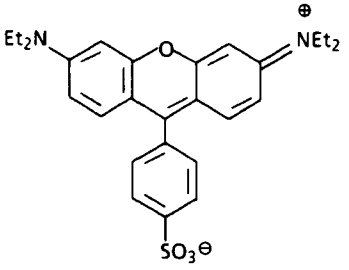

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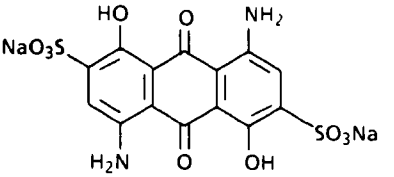
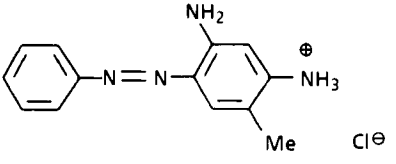
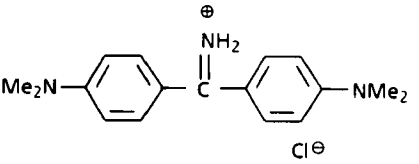


8. Acid Blue 45



9. Basic Orange 1



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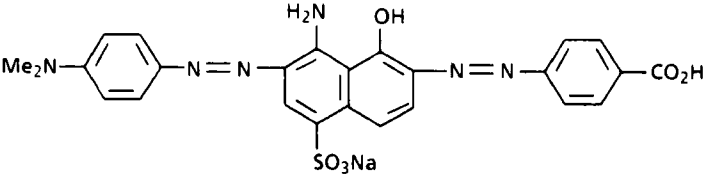

11. An Experimental Disazo Dye

Figure 1. Structures of Compounds 5-11.

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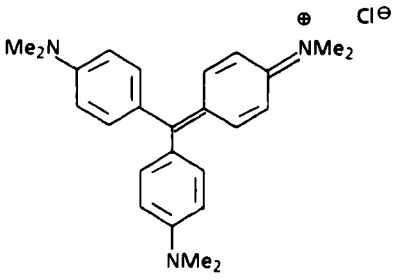
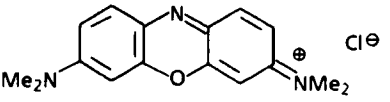
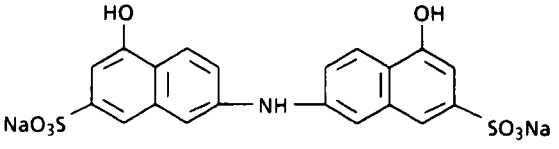


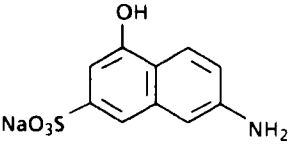

12. Basic Violet 1



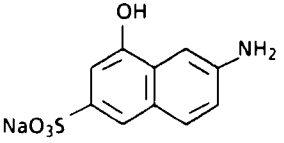

13. Basic Blue 3



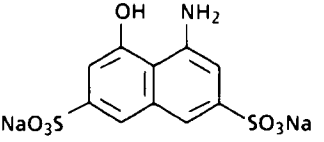

14. J-acid imide



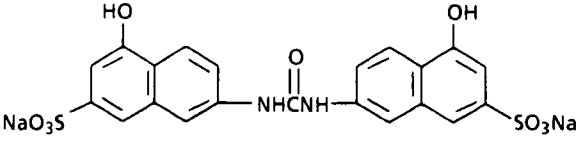

15. J-acid



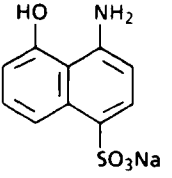

16. γ-acid




17. H-acid




18. J-acid urea




19. S-acid

Figure 2. Structures of Compounds 12-19.

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compound was spotted on TLC plates containing various forms of the cation and anion exchangers, and the plates were developed using several different eluents. The best results were obtained when EtOH:$H_2O$ (1:1) or 0.5M HOAc were used as the eluent. The results are summarized in Table 1, Table 2, and in the discussion which follows.

Cation Exchangers

CEL 300CM. On this weak cation exchanger the acid dyes (**5-8**) travelled faster and closer (similar $R_f$) on the $Na^+$ and $NH_4^+$ forms when EtOH:$H_2O$ (1:1) was the eluent. Using this eluent and exchanger, better differentiation between **5-8** was possible when the $H^+$ and $Li^+$ forms were employed (cf. Figure 3a). Three of the 4 basic dyes (**9-10, 12-13**) move at nearly the same rate on the $Na^+$, $NH_4+$, and $Li^+$ forms, but better distinction and resolution of the components occur with the $H^+$ form of this exchanger (cf. Figure 3b). Beck and coworkers (9) reported a similar specificity for separations involving durable press agents. The disazo dye **11** streaked severely on each form of the exchanger using EtOH:$H_2O$ (1:1). The naphthalenesulfonic acid derivatives (**14-19**) moved at nearly the same rate on all 4 forms of this exchanger using this same eluent (cf. Figure 3c).

When 0.5 M HOAc was used as the eluent, all of the dyes moved significantly slower (cf. Figures 4a-b) on each form of CEL 300 CM relative to their speed when EtOH:$H_2O$ (1:1) was used, with the exception Acid Red 52 on the $Li^+$ form. Interestingly, this eluent affords better differentiation between the naphthalenesulfonic

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**TABLE 1.**

**Ion Exchange Chromatography Data for Compounds 5-11**

| RESIN USED | MOBILE ION | ELUENT | $R_f$ Values 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|
| CEL 300 CM | $NH_4^+$ | EtOH:$H_2O$ (1:1) | 0.75 | 0.70 | 0.81 | 0.77 | 0.27 | 0.53 | d |
| CEL 300 CM | $Na^+$ | EtOH:$H_2O$ (1:1) | 0.80 | 0.73 | 0.90 | 0.83 | 0.63 | 0.85 | d |
| CEL 300 CM | $H^+$ | EtOH:$H_2O$ (1:1) | 0.67 | 0.65 | 0.90 | d | 0.43[c] | 0.73 | d |
| CEL 300 CM | $Li^+$ | EtOH:$H_2O$ (1:1) | 0.30 | 0.33 | 0.50 | d | 0.15 | 0.55 | d |
| FIXION 50x8 | $NH_4^+$ | 0.5 M HOAc | 0.20[c] | 0.07 | 0.10 | 0.53 | 0 | 0 | 0 |
| FIXION 50x8 | $Na^+$ | 0.5 M HOAc | 0.08[c] | 0.05 | 0.07 | 0.41 | 0 | 0 | 0 |
| FIXION 50x8 | $H^+$ | 0.5 M HOAc | 0.67[c] | 0.05 | 0.17 | 1.0 | 0 | 0 | 0 |
| FIXION 50x8 | $Li^+$ | 0.5 M HOAc | 0.33[c] | 0.08 | 0.17 | 0.85 | 0 | 0 | 0 |
| CEL 300 CM | $NH_4^+$ | 0.5 M HOAc | 0.24[c] | 0.12[c] | 0.71 | 0.13[c] | 0.05 | 0.11[c] | 0 |
| CEL 300 CM | $Na^+$ | 0.5 M HOAc | 0.20[c] | 0.10[c] | 0.78 | 0.11[c] | 0.03 | 0.13[c] | 0 |
| CEL 300 CM | $H^+$ | 0.5 M HOAc | 0.27[c] | 0.17[c] | 0.70 | d | 0.03 | 0.18[c] | 0 |
| CEL 300 CM | $Li^+$ | 0.5 M HOAc | 0.24[c] | 0.12[c] | 0.58 | d | 0.03 | 0.11[c] | 0 |
| CEL 300 DEAE | a | EtOH:$H_2O$ (1:1) | 0.43[c] | d | 0.75 | 0 | 0.37 | 0.48[c] | 0 |
| CEL 300 DEAE | b | EtOH:$H_2O$ (1:1) | d | d | 0.20[c] | 0 | 0.55 | 0.16[c] | 0 |
| FIXION 2x8 | $OAc^-$ | 0.5 M HOAc | 0 | 0 | 0 | 0 | d | d | 0 |
| FIXION 2x8 | $ClO_4^-$ | 0.5 M HOAc | 0 | 0 | 0 | 0 | d | d | 0 |
| CEL 300 DEAE | a | 0.5 M HOAc | 0 | 0 | 0 | 0 | 0.17[c] | 0.63 | 0 |
| CEL 300 DEAE | b | 0.5 M HOAc | 0 | 0 | 0 | 0 | 0.08[c] | 0.83 | 0 |

a = Untreated commercial resin.

b = $NaClO_4$ treated resin.

c = Elongated spot with center at $R_f$ indicated.

d = Streaked badly.

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**TABLE 2.**

**Ion Exchange Chromatography Data for Compounds 12-19**

| RESIN USED | MOBILE ION | ELUENT | $R_f$ Values 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|---|
| CEL 300 CM | $NH_4$+ | EtOH:$H_2O$ (1:1) | 0.55,0.48 | 0.60 | 0.38[c] | 0.67 | 0.55 | 0.55 | 0.31 | 0.55 |
| CEL 300 CM | Na+ | EtOH:$H_2O$ (1:1) | 0.85 | 0.63 | 0.78 | 0.80 | 0.81 | 0.81 | 0.63[c] | 0.81 |
| CEL 300 CM | H+ | EtOH:$H_2O$ (1:1) | 0.96,0.73 | 0.76 | 0.63[c] | 0.75 | 0.73 | 0.73 | 0.60[c] | 0.73 |
| CEL 300 CM | Li+ | EtOH:$H_2O$ (1:1) | 0.60,0.50 | 0.63 | 0.61 | 0.61 | 0.55 | 0.57 | 0.58 | 0.57 |
| FIXION 50x8 | $NH_4$+ | 0.5 M HOAc | 0 | 0 | 0.21[c] | 0.17[c] | 0.25 | 0.91 | 0.30[c] | 0.68 |
| FIXION 50x8 | Na+ | 0.5 M HOAc | 0 | 0 | 0.21[c] | 0.17[c] | 0.30 | 0.68 | 0.33[c] | 0.90 |
| FIXION 50x8 | H+ | 0.5 M HOAc | 0 | 0 | 0.25[c] | 0.21[c] | 0.24 | 0.83 | 0.30[c] | 0.83 |
| FIXION 50x8 | Li+ | 0.5 M HOAc | 0 | 0 | 0.25[c] | 0.25[c] | 0.30 | 0.65 | 0.23[c] | 0.65 |
| CEL 300 CM | $NH_4$+ | 0.5 M HOAc | 0.03 | 0.15[c] | 0.05[c] | 0.53 | 0.55 | 0.63 | 0.03[c] | 0.61[c] |
| CEL 300 CM | Na+ | 0.5 M HOAc | 0.05 | 0.13[c] | 0.05[c] | 0.61 | 0.61 | 0.77 | 0.05[c] | 0.73 |
| CEL 300 CM | H+ | 0.5 M HOAc | d | 0.13[c] | 0.05[c] | 0.60 | 0.60 | 0.83 | 0.13[c] | 0.81[c] |
| CEL 300 CM | Li+ | 0.5 M HOAc | 0.03 | 0.15[c] | 0.05[c] | 0.40 | 0.43 | 0.45 | 0.07[c] | 0.53 |
| CEL 300 DEAE | a | EtOH:$H_2O$ (1:1) | 0.55 | 0.67 | 0 | 0.17[c] | 0.13[c] | 0.05 | 0 | d |
| CEL 300 DEAE | b | EtOH:$H_2O$ (1:1) | 0.60 | 0.83 | 0 | 0.08[c] | 0.08[c] | 0.03 | 0 | d |
| FIXION 2x8 | OAc- | 0.5 M HOAc | 0.17 | 0.13[c] | 0 | 0 | 0 | 0 | 0 | d |
| FIXION 2x8 | $ClO_4$- | 0.5 M HOAc | 0.08 | 0.10[c] | 0 | 0 | 0 | 0 | 0 | d |
| CEL 300 DEAE | a | 0.5 M HOAc | d | 0.40[c] | 0 | 0.11 | 0.13[c] | 0 | 0 | 0 |
| CEL 300 DEAE | b | 0.5 M HOAc | 0 | d | 0 | 0.25 | 0.21 | 0 | 0 | 0 |

a = Untreated commercial resin.

b = $NaClO_4$ treated resin.

c = Elongated spot with center at $R_f$ indicated.

d = Streaked badly.

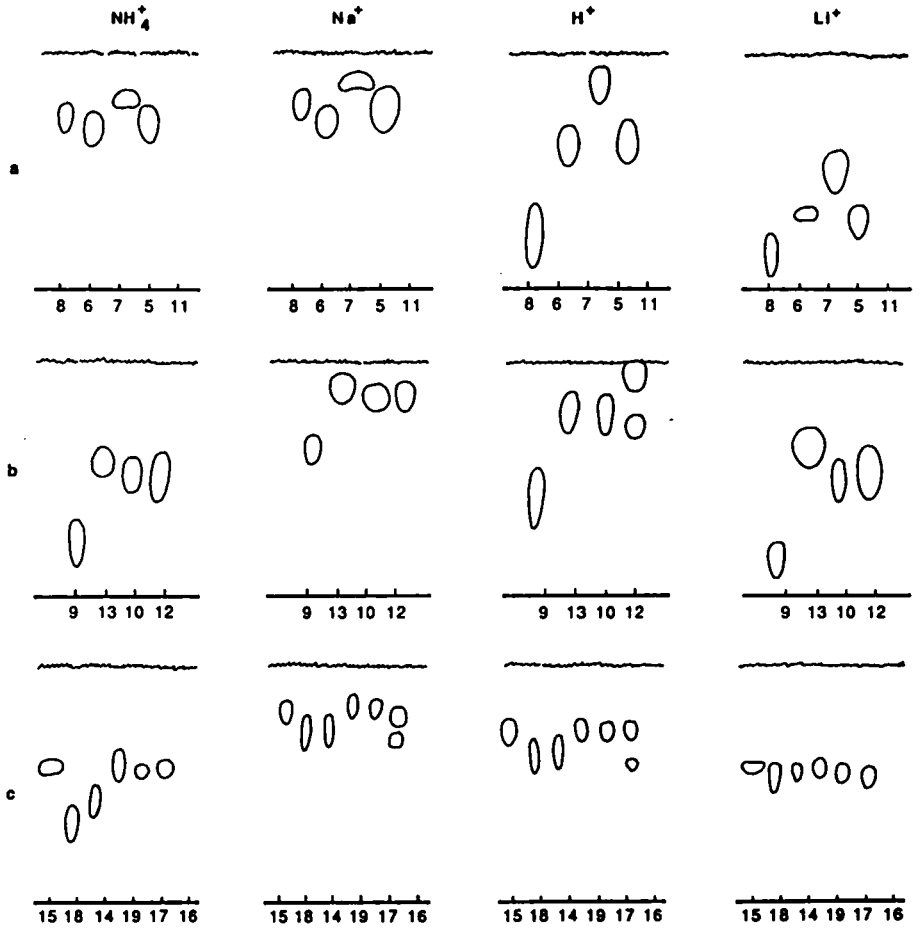


FIGURE 3. Thin layer chromatograms of some acid dyes (a), basic dyes (b), and dye intermediates (c) on various forms of CEL 300 CM using EtOH:$H_2O$ as the eluent.

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acids (cf. Figure 4c). The bisnaphthalenesulfonic acids **14** and **18** are much more retarded by this exchanger than the simpler naphthalenes. It is possible that the matrix itself contributes to the observed affinity, as it is known (10-12) that these compounds afford azo derivatives having high affinity for cellulosic substrates. The disazo dye **11** remained at the origin using this eluent.

FIXION 50x8

When EtOH:$H_2O$ (1:1) was used as the eluent on this strong cation exchanger the authors encountered problems with the layers separating from the polyester backing. This prevented a clearly reproducible direct comparison of the FIXION 50x8 and CEL 300 CM exchangers using this vehicle. However, when 0.5 M HOAc is employed as the eluent some interesting differences in the behavior of all of the compounds on this exchanger relative to the weak cation exchanger are clearly evident. For instance, the form of this exchanger greatly effects the $R_f$ value of the acid blue (**8**) and orange (**5**) dyes. Whereas dye **7** moves faster than **5** and **8** using 0.5 M HOAc on the weak cation exchanger, the latter two dyes move faster than **7** on the strong cation exchanger (Fixion 50x8). Also, the $H^+$ and $Li^+$ forms of this strong cation exchanger afforded faster movement of the acid dyes (cf. Figure 5a), in contrast to the results obtained on CEL 300 CM.

FIXION 50x8 also permits differentiation between the individual naphthalenesulfonic acids **14-19** (cf. Figure 5b). Unlike the acid dyes, these compounds have comparable behavior on

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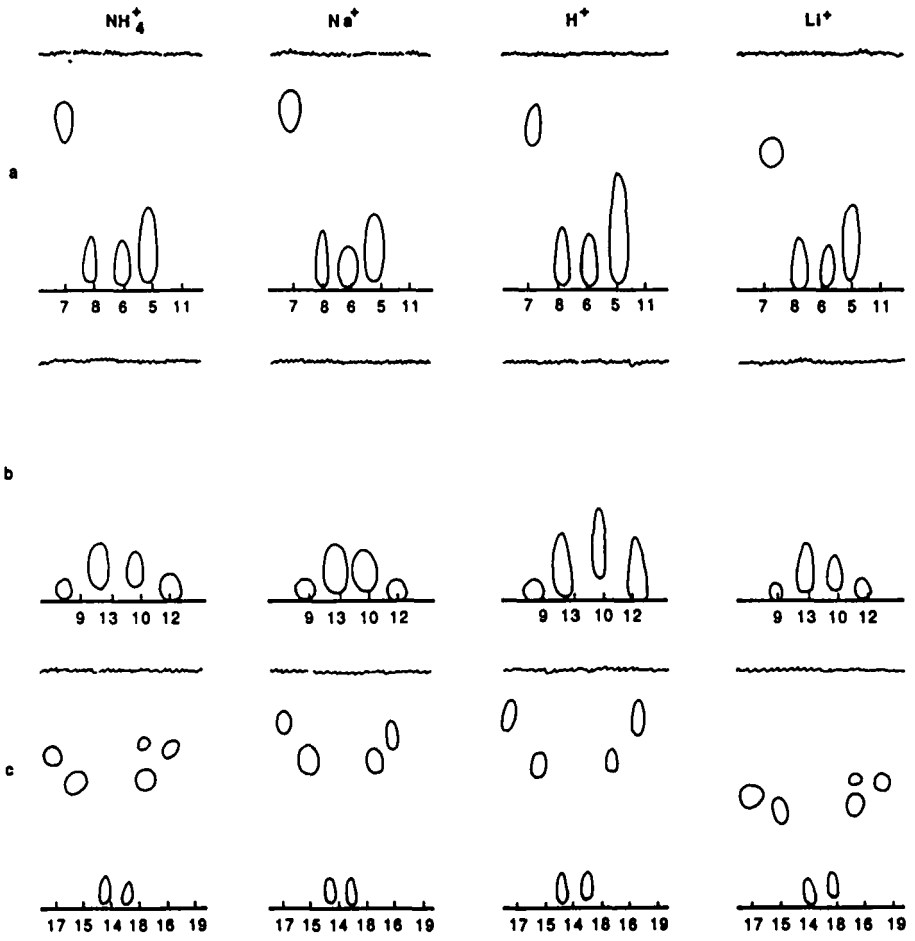


FIGURE 4. Thin layer chromatograms of some acid dyes (a), basic dyes (b), and dye intermediates (c) on various forms of CEL 300 CM using 0.5 M HOAc as the eluent.

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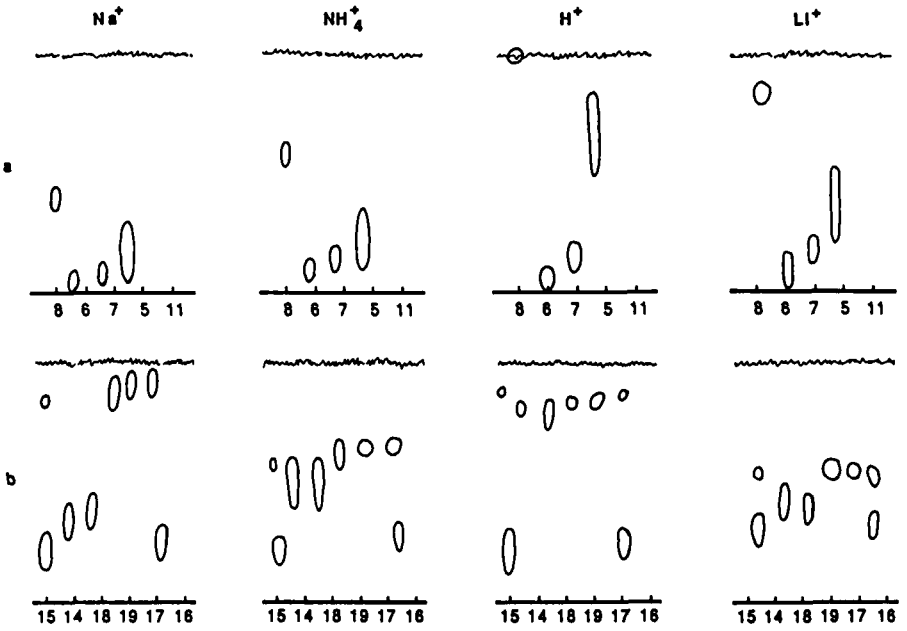


Figure 5. Thin layer chromatograms of acid dyes (a) and dye intermediates (b) on various forms of FIXION 50x8 using 0.5 M HOAc as the eluent.

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the strong and weak cation exchangers when 0.5 M HOAc is the eluent.

The basic dyes do not move on FIXION 50x8 when 0.5 M HOAc is used, regardless of the form of the exchanger.

Anion Exchangers

FIXION 2x8. This strong anion exchanger prevents the movement of the acid dyes and the dye intermediates when either 0.5 M HOAc, 0.001 M NaOH, or a solvent useful in the development of these compounds on silica plates is employed, regardless of the form

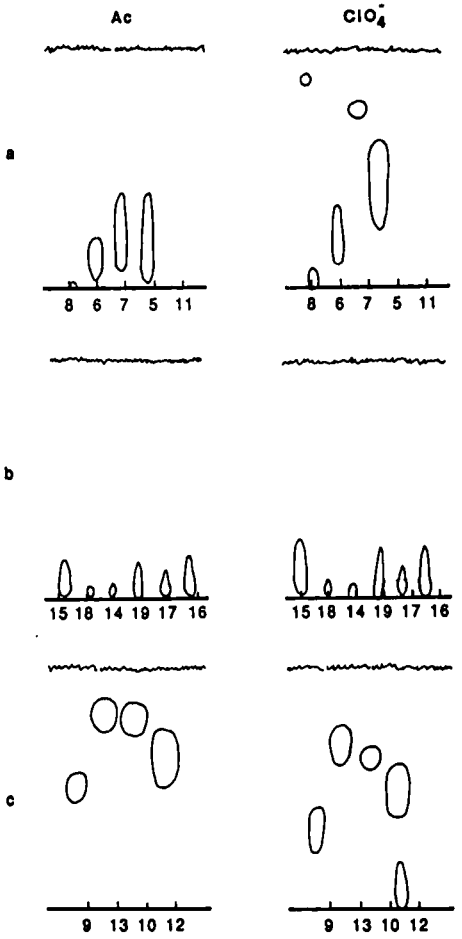


Figure 6. Thin layer chromatograms of acid dyes (a), basic dyes (b) and dye intermediates (c) on untreated and $NaClO_4$ treated CEL 300 DEAE using EtOH:$H_2O$ (1:1) as the eluent.

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($ClO_4^-$, $OAc^-$, citrate) of the exchanger. Little movement of the basic dyes is evident under the same conditions.

This exchanger does not appear to be useful for any class of hydrophilic dyes, as it binds each too tightly.

CEL 300 DEAE. On this weak anion exchanger the use of 0.5 M HOAc essentially prevents the movement of the acid dyes and the dye intermediates. Although the cationic dyes move under these conditions, elongated spots are produced.

When EtOH:$H_2O$ (1:1) is used, the acid blue dye and compounds **14-19** remain near the origin. However, the other 3 acid dyes and the basic dyes chromatograph (cf. Figure 6).

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## CONCLUSIONS

It has been shown that thin layers of ion exchangers are useful substrates for evaluating relatively low molecular weight hydrophilic dyes and dye intermediates. It has also been demonstrated that both the binding strength of the enchanger and the mobile ion greatly effect the resolution of components in a dye mixture as well as the ability to differentiate between structurally similar dyes and intermediates. Moreover, the results of this study indicate that 0.5 M HOAc is a good all-around eluent for acid dyes on strong and weak cation exchangers, and for sulfonated naphthalenes on cation exchangers. For the basic dyes, the best combinations seem to be EtOH:$H_2O$ (1:1) on the weak cation or anion exchangers.

## ACKNOWLEDGEMENTS

The authors wish to thank Mr. Mark Bowen for his artwork in the figures of this paper.

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