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Short communication

Adsorption chromatography on cellulose XIV. Some results using aqueous solutions of soluble cyclodextrin polymers as eluents

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Abstract

Commercial α-, β- and γ-cyclodextrin polymers were examined for their eluent properties in adsorption chromatography on cellulose thin layers using aqueous solvents. Azo dyes were found to be eluted better by the polymers than by a solution of α-cyclodextrin. Chloroauric acid ($HAuCl_4$) was eluted on the liquid front by polymers but not by α-cyclodextrin. No improvement could be seen in the separation of tryptophan enantiomers compared with α-cyclodextrin. α-Cyclodextrin (monomer) yields much better separations than any of the polymers. Attempts to use the polymers as non-specific desorbing agents for coloured inks were unsuccessful.

Keywords: Cellulose; Cylodextrins; Tryptophan; Chloroauric acid; Azo dyes

1. Introduction

In our studies on adsorption chromatography on cellulose, we have obtained interesting results when aqueous cyclodextrin solutions were used as eluents [1,2]. The chiral effect of cellulose could be increased for the separation of D,L-tryptophan and some of its derivatives when solutions of α-cyclodextrin were used as eluents [1]. Both β- and γ-cyclodextrin are strongly adsorbed on cellulose and thus do not migrate with the solvent front. In our previous studies we have not done much work with β-cyclodextrin for this reason.

Recently, our attention was drawn to a series of cyclodextrin polymers manufactured by Cyclolab (Budapest, Hungary) which are very soluble in water (30–40%) and which are recommended as "solubilizers". In this paper, the behaviour of these polymers when used as additives to an aqueous solvent in cellulose thin-layer chromatography is considered.

2. Experimental

Merck No. 5577 cellulose thin layers were used. α-Cyclodextrin and β-cyclodextrin were obtained from Fluka (Buchs, Switzerland). The following cyclodextrin polymers cross-linked

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with 1-chloro-2,3-epoxypropane were obtained from Cyclolab: CY-1009, soluble α-cyclodextrin polymer, $M_r = 3500$, solubility in water >40%, solubilizer CD content, 50–60%; CY-2009, soluble β-cyclodextrin polymer, $M_r = 3000–5000$, solubility in water >40%, insoluble in benzene; solubilizer CD content, 50–60%; and CY-3009, soluble γ-cyclodextrin polymer, $M_r = 3000–5000$, solubility in water >33%, insoluble in benzene; solubilizer CD content, 50–60%.

The development chambers were small plastic jars (65 mm diameter, height 100 mm). Usually the required amount of the cyclodextrin polymer, e.g., 100 mg, was weighed into these jars on an analytical balance and 10 ml of 1 M NaCl solution were added. Development was carried out at room temperature (20–22°C).

3. Results

3.1. Azo dyes

In our previous work with α-cyclodextrin [2], we reported a strong desorption of Methyl Orange and Ethyl Orange from cellulose when the solution contained α-cyclodextrin. As shown in Table 1, α-cyclodextrin polymer has a similar even perhaps better desorption effect.

In acidic or alkaline solutions, α-cyclodextrin polymer also exhibits better desorption effects than α-cyclodextrin, as shown in Table 2.

When the R_F values are in the intermediate range there is a good linear correlation between the R_M values and log(concentration of α-cyclodextrin polymer) in the eluent. In Fig. 1 Methyl Red has three data points (0.08, 0.09 and 0.13) of low precision and this may account for the non-linearity.

Table 3 shows a comparison of the three (α-, β- and γ-) cyclodextrin polymers as eluents for azo dyes. There are several interesting differences, e.g., Methyl Yellow has a stronger affinity to the α-cyclodextrin polymer and Ethyl Red a weaker affinity, but on the whole the effects are not very different.

3.2. Metal complexes

Amongst the usual chloro complexes of metal ions stable in aqueous HCl, only one, $HAuCl_4$, is

Table 2
R_F values of azo dyes on microcrystalline cellulose thin layers (Merck 5577) with 0.5 M HCl and 1 M Na_2CO_3 solution in the presence of 1% of α-cyclodextrin and 1% α-cyclodextrin polymer at room temperature

Azo dye	0.5 M HCl		1 M Na_2CO_3	
	α-CD polymer	α-CD	α-CD polymer	α-CD
Methyl Orange	1.00	0.77	0.89	0.72
Methyl Red	0.38	0.17	0.30	0.14
Methyl Yellow	0.92	0.73	0.69	0.40
Ethyl Orange	1.00	0.97	0.91	0.73
Ethyl Red	0.66	0.35	0.68	0.23
Alizarin Yellow R	0.71	0.22	0.70	0.43
Alizarin Yellow 2G	0.80	0.00	0.70	0.51

Table 1
R_F values of Methyl Orange and Ethyl Orange on microcrystalline cellulose thin layers (Merck 5577) with 1 M NaCl solution in the presence of various concentrations of α-cyclodextrin or cyclodextrin polymers at room temperature

α-CD or α-CD polymer concentration (%)	Methyl Orange		Ethyl Orange	
	α-CD	α-CD polymer	α-CD	α-CD polymer
0.01	0.18	0.13	0.46	0.53
0.05	0.35	0.44	0.64	0.58
0.10	0.45	0.60	0.81	0.76
0.25	0.69	1.00	0.85	0.99
0.50	–	1.00	–	1.00
1.00	0.90	1.00	0.86	1.00

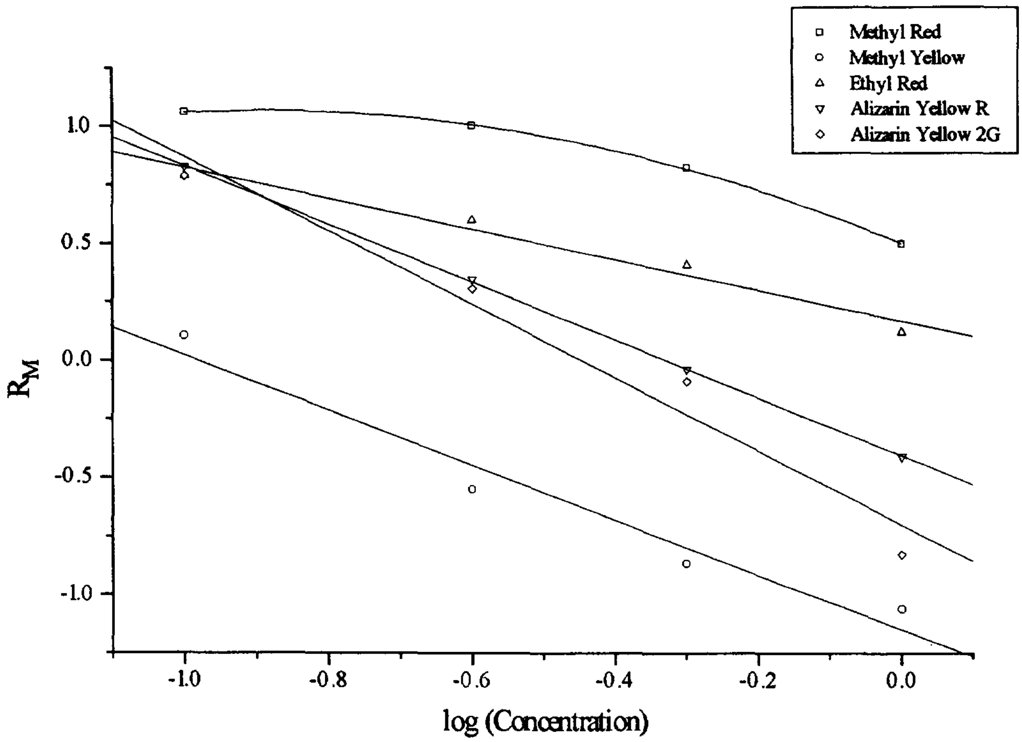

Fig. 1. R_M values of azo dyes plotted against log(concentration of α-cyclodextrin polymer) in 1 *M* NaCl as solvent.

adsorbed on cellulose [3]. In our work with cyclodextrins we tried to establish whether these desorb chloroauric acid from cellulose but did not observe any effect. The cyclodextrin polymers did, however, show a marked effect. While $HAuCl_4$ has an R_F value of 0.49 on cellulose developed with 1 *M* NaCl and with 1 *M* NaCl containing α-cyclodextrin, it is eluted with R_F values of 0.69, 0.98 and 0.98 with 1 *M* NaCl containing α-CD polymer, β-CD polymer and

Table 3
R_F values of azo dyes on microcrystalline cellulose thin layers (Merck 5577) with 1 *M* NaCl solution in the absence and in presence of 0.5% of cyclodextrin polymers at room temperature

Azo dye	R_F			
	1 *M* NaCl	0.5% α-cyclodextrin polymer	0.5% β-cyclodextrin polymer	0.5% γ-cyclodextrin polymer
Methyl Orange	0.1	1.00	0.8	0.79
Methyl Red	0.08	0.13	0.24	0.23
Methyl Yellow	0.00	0.88	0.55	0.54
Ethyl Orange	0.44	1.00	0.97	1.00
Ethyl Red	0.12	0.28	0.50	0.48
Alizarin Yellow R	0.00	0.52	0.43	0.41
Alizarin Yellow 2G	0.03	0.55	0.48	0.61

γ-CD polymer, respectively. *cis*-$Pt(II)(NH_3)_2Cl_2$, on the other hand, has essentially the same R_F value (0.7) with all these eluents.

3.3. Separation of enantiomers

In the separation of enantiomers of tryptophan and methyltryptophan, the addition of α-cyclodextrin to the aqueous eluent yielded better separations, some with separation factors better than those achieved by other methods [1]. The cyclodextrin polymers proved disappointing. As shown in Table 4, the R_F differences are usually less than when α-cyclodextrin is added to the eluent.

With α-cyclodextrin we had previously observed an intense and highly sensitive blue-black coloration of the tryptophan on the thin layers when these were exposed to iodine vapour [1]. Cyclodextrin polymers do not give this reaction, so ninhydrin was used to reveal the tryptophan spots. After the much greater effects noted above with azo dyes, we find it remarkable that the enantiomeric separations produced by cyclodextrin polymers are rather mediocre.

3.4. Polymerized cylcodextrins as "solubilizers"

The manufacturer (Cyclolab) recommends the polymerized cyclodextrins as solubilizers. There is an interest in desorbing dyestuffs from cellulose, e.g., in the forensic identification of inks, hence experiments examining a range of coloured felt pens and other pens using 1 *M* NaCl with 1% additions of α-CD and the three CD polymers were carried out. For a number of the felt-pen dyes the movement varied considerably with the cyclodextrin in the eluent, but in no case could one speak of non-specific and strong elution of all the dyestuffs. Hence elution with cyclodextrin polymers cannot be recommended as a non-specific elution strong enough to desorb unknown dyestuffs from cellulose.

4. Conclusion

The soluble cyclodextrin polymers have shown some interesting features when used in the eluent in adsorption chromatography on cellulose. Azo dyes are more strongly desorbed than with α-CD. Chlorauric acid is desorbed by the polymers but not at all by α-CDs. On the other hand, the

Table 4
R_F values of enantiomers of tryptophan and its derivatives on microcrystalline cellulose thin layers (Merck No. 5577) with 1 *M* NaCl solution in the absence and presence of α-cyclodextrin and cyclodextrin polymers at room temperature

Compound	R_F									
	1 *M* NaCl		4% α-cyclodextrin		4% α-cyclodextrin polymer		4% β-cyclodextrin polymer		4% γ-cyclodextrin polymer	
	L	D	L	D	L	D	L	D	L	D
Tryptophan	0.39	0.45	0.49	0.58	0.61	0.61	0.51	0.58	0.49	0.56
l-Methyltryptophan	0.38	0.45	0.46	0.56	0.65	0.65	0.49	0.58	0.48	0.56
4-Methyltryptophan	0.23	0.32	0.26	0.36	0.39	0.50	0.35	0.48	0.30	0.41
5-Methyltryptophan	0.25	0.32	0.42	0.52	0.55	0.62	0.41	0.51	0.38	0.49
6-Methyltryptophan	0.25	0.31	0.47	0.62	–[a]	–[a]	0.46	0.55	0.43	0.53
7-Methyltryptophan	0.29	0.35	0.30	0.38	0.43	0.52	0.44	0.49	0.39	0.46
4-Fluorotryptophan	0.34	0.41	0.38	0.48	0.51	0.69	0.46	0.56	0.44	0.54
5-Fuorotryptophan	0.35	0.40	0.44	0.52	0.69	0.69	0.51	0.58	0.47	0.55
6-Fluorotryptophan	0.34	0.41	0.48	0.64	–[a]	–[a]	0.51	0.60	0.49	0.59

Spots were detected with iodine vapour for α-cyclodextrin and with 1% ninhydrin in acetone for the others.
[a] Could not be detected.

enantiomers of tryptophan derivatives do not separate better than with α-CD in the systems tried by us, nor can the polymers be considered as general "solubilizers".

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