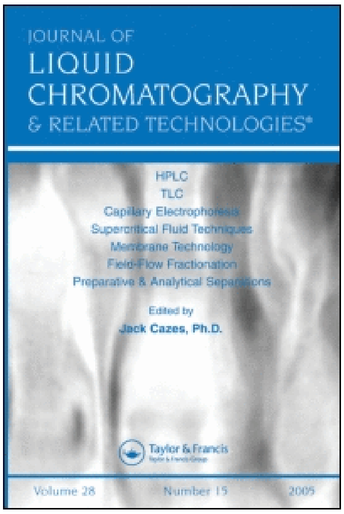

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SORPTION OF ACIDS, AND FORMATION OF HYDROGEN ION AND ANION FRONTS ON A THIN LAYER

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ABSTRACT

The behavior of acids on the layers of cellulose and silica gel was studied. The samples used were HCl and $HClO_4$, and the developers were water, acetone, ethanol, and n-butanol. Monitored, was also the behavior of HCl as a component of the developers water-HCl and n-butanol-HCl. The results have shown that acids are strongly sorbed on the layers of silica gel and cellulose. Hydrogen ion and an anion of strong inorganic acids behaved differently on sorbent layer; generally H^+ ion was stronger sorbed than A^- ion. Sorption and behavior of acid ions depended on the properties of a sorbent, solvent and acid, i. e. on an interaction of all components of the chromatographic system.

Developers with a low content of a strong acid formed on the chromatogram two or three fronts: $F_{solvent}$, F_{A}^{-} and F_{H}^{+}, and two or three areas of different composition of a developer and sorbed ions, in which areas there was a gradient of H^+ and A^- concentration. Weak acids were bound to the layer as molecules and could produce a second front (F_{HA}) only.

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INTRODUCTION

Acids, inorganic, and organic, are employed in chromatography as components of a developer, especially in the planar chromatography of inorganic substances. They play in it an important role and facilitate separation of compounds or ions in a mixture. Some researchers thought that the acids did not bind on the paper, or on a thin layer of sorbent, but travel during the development with the solvent front.[1,2]

Appearance of the so called "second front" on the paper and on a thin layer was observed a long time ago. It was associated with the employment of the developers containing a strong acid (e.g. HCl). The second front was initially regarded a front which water molecules reached on a chromatogram, because the polar molecules of water were thought to bind primarily to a layer. It was then perceived that the acid effected the height of the second front, and that its height was being increased by an increased acid content of a developer.[3,4] Later it was established that the second front was a chromatogram line to which the acid molecules arrive.[5]

Present work was aimed to study the behavior of the acids on thin layers of cellulose and silica gel with respect to the solvent employed as a developer. The results have shown marked sorption of acids on thin layers and the difference in sorption between hydrogen ion and an anion of a strong acid.

EXPERIMENTAL

The experiments were carried out on the layers of microcrystalline cellulose for TLC (E. Merck) and silica gel 60 GF_{254} (E. Merck). Thin layers were laboratory prepared.

Preparation of Layers

Water suspensions (cellulose + water = 1:2.5 and silica gel + water = 1:2) were spread over glass plates by means of CAMAG apparatus. Thickness of layer was 0.2 mm. The layers were allowed to air-dry (overnight).

Testing Samples

Solutions of HCl and $HClO_4$; concentration of acids: $c(HCl) = 6$ mmol/mL $c(HClO_4) = 3.5$ mmol/mL. Applied volume of the sample solution: 20-30 μL.

Developers

Water, acetone, ethanol, and n-butanol for development of HCl and $HClO_4$ samples. Water-HCl conc. (40 + 0.5, v/v) and n-butanol-HCl conc. (40 + 0.5, v/v) for the purpose of studying the behaviour of strong acid (HCl) as a developer component.

Development

The development was performed in Camag chromatographic chamber, by ascending technique, along 10 cm line. Samples of the acids were spotted to the plates, dried, and then chromatographed. After development, the plates were dried and sprayed with corresponding reagents.

Reagents for Detection

Methyl orange 0.1 g in 100 mL of water; K_2CrO_4 5.0 g in 100 mL of water; $AgNO_3$ 0.25 mol/L, water solution acidified with HNO_3; methylene blue 2 g in 100 mL of water, solution saturated with $ZnSO_4$.

Detection

H^+ was detected by spraying with methyl orange; Cl^- by spraying with $AgNO_3$ and than with K_2CrO_4; ClO_4^- by spraying with methylene blue.

RESULTS AND DISCUSSION

Results of chromatographic behaviour of HCl and $HClO_4$ as samples are presented in Tables 1 and 2. The results show that HCl and $HClO_4$ were markedly sorbed on the cellulose and silica gel layers.

There was also a marked difference in mobility (i. e. sorption) between H^+ ion and Cl^- ion, as well as between H^+ ion and ClO_4^- ion on both sorbents.

As regards HCl behaviour (Table 1) it is evident that sorption of H^+ ion was somewhat higher than of Cl^- ion with water and ethanol as developers, while Cl^- ion showed slightly superior sorption when developed with acetone and n-butanol on cellulose layer. Development of HCl samples on silica gel layer with all tested solvents caused significantly stronger sorption of H^+ ion than of Cl^- ion, which resulted in nearly complete separation of Cl^- ion from H^+ ion mass.

Table 1

Behaviour of Hydrochloric Acid on Cellulose and Silica Gel Thin Layers

	R_f Values			
	Cellulose		**Silica Gel**	
Developer	**H^+**	**Cl^-**	**H^+**	**Cl^-**
Water	0.35-1 (0.6-1)*	0.63-1	0-0.75	0.3-1 (0.8-1)*
Acetone	0-0.75	0-0.7	0-0l.61	0-0.85 (0.5-0.85)*
Ethanol	0.2-1 (0.5-1)*	0-1 (0.7-1)*	0-0.65 (0.4-0.65)*	0.56-0.86
n-Butanol	0-0.78	0-0.72	0.0.66	0-0.80 (0.35-0.8)*

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* main part of ion amount.

Table 2

Behaviour of Perchloric Acid on Cellulose and Silica Gel Thin Layers

	R_f Values			
	Cellulose		**Silica Gel**	
Developer	**H^+**	**ClO_4^-**	**H^+**	**ClO_4^-**
Water	0-1 (0.8-1)*	0.96-1	0-0.90 (0.77-0.9)*	0.79-1
Acetone	0-0.97	0-0.97	0-0.80 (0.6-0.8)*	0.65-0.93
Ethanol	0-1 (0.65-1)*	0.2-1	0-0.78	0.66-0.94
n-Butanol	0-0.90 (0.25-0.9)*	0-0.90	0-0.85 (0.66-0.85)*	0.62-0.91

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* main part of ion amount.

Consequently, a major part of the Cl^- ion was anterior to the mass of a hydrogen ion (lower part of elongated spot contained H^+ only, and the upper part Cl^- only).

When $HClO_4$ sample was chromatographed (Table 2), on cellulose layer, H^+ ion was considerably sorbed with water as a developer, whereas ClO_4^- traveled with the water front (separating almost completely from H^+). Development with acetone, ethanol, and n-butanol produced similar behavior of H^+ and of ClO_4^- ions on cellulose layer; both were sorbed, mostly with n-butanol (solvent with the lowest polarity).

$HClO_4$ on silica gel layer behaved analogously to hydrochloric acid: significantly stronger sorption of H^+ ion produced marked separation of ClO_4^- ion (appearing in the upper part of the elongated spot). However, ClO_4^- and Cl^- ions exhibited a certain degree of sorption on silica gel layer and did not migrate to the solvent front.

Comparison of the results (Tables 1 and 2) showed significant differences in the behavior of the acids on cellulose compared to the silica gel layer. Particularly notable was stronger sorption of H^+ on silica gel than on cellulose. There was also the difference in anion sorption. These facts indicated the dependency of acid ion sorption on sorptive property of the sorbent.

Correlation in the chromatographic behavior of acid ions and properties of the solvent used as a developer was particularly evident from the comparison of the behavior of acids developed with water and n-butanol; sorption, especially of acid anions, was much lower in case of water, whereas with n-butanol it was the highest. Consequently, dependence of acid sorption on the solvent polarity (and other solvent properties, which affects ascending velocity, miscibility, and contact with sorbent layer) was evident.

Differences in behavior of HCl and $HClO_4$ indicated that the behavior of an acid was related to its properties, or properties of its ions. Hence, sorption of the acids on a thin layer was influenced by all components of the chromatographic system, i. e., by sorbent-acid-solvent interaction.

Another series of experiments employed the strong acid (HCl) as the component of a developer. The behaviour of HCl in developers was in agreement with results obtained for the sorption (Table 1). Developer water - conc. HCl (40 + 0.5, v/v) formed two fronts: hydrogen ion front and common front of water and chloride ion on cellulose layer and on silica gel layer as a sorbent. Due to the stronger sorption of H^+ ion on silica gel rather than on cellulose, the H^+ ion front on silica gel layer was lower than on cellulose.

HCl exhibited different behavior on cellulose and on silica gel layers when n-butanol-conc. HCl (40 + 0.5, v/v) was a developer. F_H^+ and F_{Cl}^- appeared on both layers, but their heights were significantly different: unlike on cellulose layer, F_H^+ was much lower on silica gel, and F_{Cl}^- appeared to be considerably higher. Moreover, chloride ion front on cellulose was slightly lower than hydrogen ion front.

These results showed that the second front, frequently manifested on the planar chromatogram during development with solvent systems containing a strong acid, was a line reached by H^+ ion. Possible, is also the occurrence of the third front (usually invisible during detection), i. e. of the line reached by an acid anion. F_H^+ and F_A^- were the outcome of a much stronger sorption of H^+ and A^- ions on the layer, compared to other molecules of a developer. The height of these fronts was dependent on the level of acid ions sorption under given chromatographic conditions. The developers having been mostly solvent mixtures (organic solvent-water-acid), position of F_H+ and F_A^- was affected by the composition of a developer (volume fraction of each component).

It can be concluded that there were three limited areas which could occur on the chromatogram depending on the ions and molecules bound to the layer: the area containing solvent molecules plus H^+ and A^- ions, the area containing solvent molecules and A^- ion or H^+ ion, and the area containing solvent molecules only. Due to the marked sorption, it was clear that the concentration of acid ions in the mentioned areas could not be uniform. It had a falling trend, both on the layer and in the mobile phase, with the increase in height during development, so there was the concentration gradient of H^+ ion and A^- ion. The well-known appearance of concentration gradient of the solvent[6] in the case of sorption of strong acids was particularly expressed, because acid ions exhibited the strongest sorption of all other molecules of the developer.

Not only strong acids, but the weak too, were sorbed on thin layers of cellulose and silica gel. It was experimentally proved that the developers with a low content of acetic acid also formed the second front. However, these acids as weakly ionized, were sorbed as molecules and formed, on the layer, an acid front as the second front (F_{HA}).

REFERENCES

1. E. Gagliardi, B. Brodar, Chromatographia, **2(4)**, 267-272 (1969).

2. H. W. Kohlschitter, C. Schäffer, Z. Anal. Chem., **245**, 129-134 (1969).

3. F. H. McOmie, J. W. F. Pollard, **Chromatographic Methods of Inorganic Analysis**, Butterworths, London, 1953.

4. F. D. Hougton, J. Chromatog., **24**, 494-498 (1966).

5. Z. Šoljić, V. Grba, Naučno-tehnički pregled, **26(2)**, 31-36 (1976).

6. F. Poole, S. K. Poole, **Chromatography Today**, Ch. 7, Elsevier, Amsterdam, 1991, pp. 655-667.

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