Some Considerations on the Role of Water in Thin Layer Chromatography of Inorganic Anions

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The volume ratios of the mobile and stationary phases in thin layer chromatography, and the partition coefficients of halide and halate anions and some other anions between these phases were obtained by developing the ions simultaneously with a series of metaphosphates. The water contents of the developing solvents influenced the volume ratios very much, but not so much the partition coefficients. The logarithm of the partition coefficient of the halide anions is proportional to the reciprocal of their ionic radius, and that of the halate anions and oxoanions to the partial charge on the oxygens of them.

Introduction

For chromatographic separations of inorganic anions, developing solvents such as mixtures of organic liquids and concentrated ammonia water are usually used. The R_f values

$$\left(R_\mathrm{f} = \frac{\text{distance travelled by the spot}}{\text{distance travelled by solvent front}}\right)$$

are very much influenced by the water content of the developing solvent, larger water contents leading to greater R_f values.

In general, the R_f values are determined by the volume ratio of the mobile and stationary phases, $A_\mathrm{m}/A_\mathrm{s}$, and the partition coefficient of the compounds between the two phases, α

$$\left(\alpha = \frac{\text{conc. in stationary phase}}{\text{conc. in mobile phase}}\right):$$

The equations $k' = \alpha \dfrac{A_\mathrm{s}}{A_\mathrm{m}}$ and $k' = \dfrac{1}{R_\mathrm{f}} - 1$ lead to the relation

$$\log(1/R_\mathrm{f} - 1) = -\log(A_\mathrm{m}/A_\mathrm{s}) + \log\alpha\,.$$

So the chromatographic behaviour depends on two parameters.

We have already reported [1] that, if we plot the R_m values ($R_\mathrm{m} = \log(1/R_\mathrm{f} - 1)$) vs. the degree of condensation of metaphosphates (consisting of m middle units), we can obtain the two parameters separately using the relationship

$$R_{\mathrm{m}\,(\text{m-meta})} = -\log(A_\mathrm{m}/A_\mathrm{s}) + m\log\alpha_{(\text{middle})}\,.$$

When we develop inorganic anions and mixtures of metaphosphates on the same thin layer plate, we can calculate α of each inorganic anion using $A_\mathrm{m}/A_\mathrm{s}$ obtained from the above mentioned plot.

$A_\mathrm{m}/A_\mathrm{s}$ is thought to be very much influenced by the properties of the developing solvent, and α may be very much influenced by the interactions of the inorganic anions with the developing solvent and the thin layer material. In these cases, water in the developing solvent plays an important role. In the present paper we investigate the role of water in the developing solvent in thin layer chromatography of inorganic anions.

Experimental

TLC cellulose plates precoated (without fluorescent indicator, Art. 5716 (Merck)) and TLC Avicel SF plates precoated (Funakoshi) were used. As samples of inorganic anions, aqueous solutions of KF, NaCl, KBr, KI, $KClO_3$, $KBrO_3$, KIO_3, $HClO_4$, K_2CrO_4, Na_2HPO_4 were prepared.

The solution of mixed metaphosphates was prepared according to Thilo and Schülke [2].

We used three kinds of developing solvents:

a) A mixture of 28 wt% NH_3 with water (60 ml) + acetone (130 ml) + *n*-butanol (30 ml);
b) Mixture a) + 20 ml of water;
c) Mixture a) + 40 ml of water.

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Each solution has been applied on the thin layer (1 µl each). The thin layer was allowed to equilibrate with the vapor of the developing solvent for three hours in a saturation chamber on the wall of which filter papers were flapped, then the inorganic anions and metaphosphates were developed. The temperature was maintained at 5 °C in an air bath (TABAI).

When the developing solvent had run for 10 cm from the point of application, the plate was taken out and dried in air. The phosphates were hydrolyzed with aqueous nitric acid (1:1) and visualized with ammonium molybdate and stanneous chloride. Halate anions were detected by the isolation of I_2 when spraying a HCl solution of KI (2%); the other anions were detected by the aluminum-morin fluorescence method.

Results and Discussion

R_f values of the metaphosphate and halide anions on TLC Avicel SF plates precoated are shown in Table 1. R_f values of the metaphosphate and halate anions on TLC cellulose plates precoated are shown in Table 2. From R_m vs. degree of condensation plots of the metaphosphates, A_m/A_s and α of middle units are obtained. Using these values, α of inorganic anions is obtained. In this time, the uniformity of A_m/A_s is inevitable, but it is thought that this condition may be satisfied to a great extend by equilibrating the TLC plates with the vapour of the developing solvents for 3 h before development. They are also shown in Tables 1 and 2. The differences of the chromatographic behavior on Funakoshi's plates and Merck's plates is thought to be only slight.

The R_f values of inorganic anions become larger with increasing water content of the developing solvents. The log (A_m/A_s) and log α vs. the volume of added water plots are shown in Figs. 1 and 2. It is shown that the increase of the R_f values is mainly due to the increase of A_m/A_s, although a slight change of α might be seen. Evidently the volume of

Table 1. Values of R_f, log (A_m/A_s) and log α obtained on Funakoshi's plate.

Solvent		a)	b)	c)
R_f Phosphates	(3 meta)	0.07	0.13	0.33
	(4 meta)	0.03–0.04	0.06–0.07	0.20
	(5 meta)	0.01–0.02	0.04–0.05	0.14
	(6 meta)		0.02–0.03	0.10
	(7 meta)			0.07
	(8 meta)			0.05
	(9 meta)			0.03
F^-		0.09	0.12	0.21
Cl^-		0.38	0.42	0.51
Br^-		0.45	0.52	0.63
I^-		0.74	0.76	0.79
log (A_m/A_s)		−0.20	−0.10	0.10
log α	PO_3^-	0.32	0.23	0.18
	F^-	0.80	0.77	0.68
	Cl^-	0.01	0.04	0.08
	Br^-	−0.11	−0.13	−0.13
	I^-	−0.65	−0.60	−0.48

Table 2. Values of R_f, log (A_m/A_s) and log α obtained on Merck's plate.

Solvent		a)	b)	c)
R_f Phosphates	(3 meta)	0.06	0.16	0.36
	(4 meta)	0.03	0.08	0.20
	(5 meta)	0.01–0.02	0.05	0.15
	(6 meta)		0.03	0.12
	(7 meta)			0.09
	(8 meta)			0.06
ClO_3^-		0.60	0.67	0.73
BrO_3^-		0.43	0.48	0.57
IO_3^-		0.06	0.09	0.13
log (A_m/A_s)		−0.20	−0.10	0.10
log α	PO_3^-	0.32	0.23	0.18
	ClO_3^-	−0.38	−0.38	−0.33
	BrO_3^-	−0.08	−0.07	−0.02
	IO_3^-	0.99	0.90	0.93

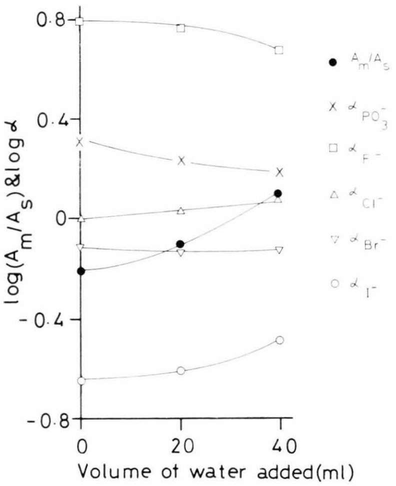

Fig. 1. Plots of log (A_m/A_s) and log α of halide anions vs. volume of water added to solvent a).

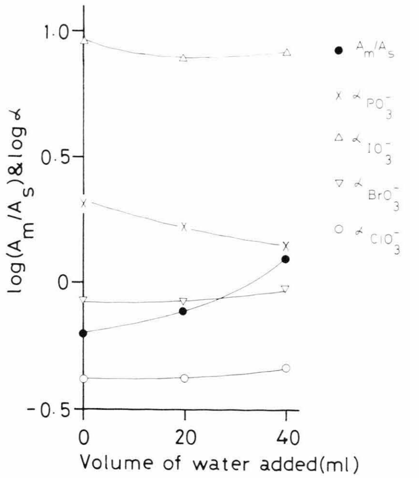

Fig. 2. Plots of $\log(A_m/A_s)$ and $\log\alpha$ of halate anions vs. volume of water added to solvent a).

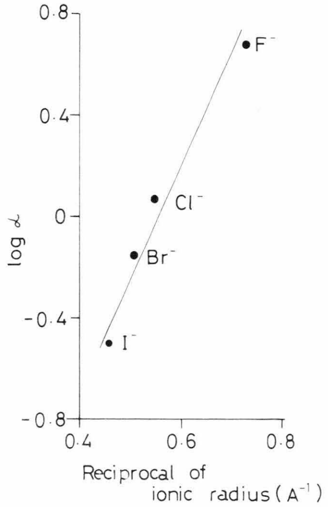

Fig. 3. Plot of $\log\alpha$ of halide anions vs. reciprocal of its ionic radius.

the stationary phase (that is the water fixed to the cellulose) does not much increase with increasing water content of the developing solvent.

The order of the R_f values of the halide anions is

$$F^- < Cl^- < Br^- < I^-,$$

but that of halate anions is

$$ClO_3^- > BrO_3^- > IO_3^-.$$

If we plot $\log\alpha$ vs. $1/r$ (r = Pauling radius) of the halide anions, we obtain a linear relationship (Figure 3). In the case of the halate anions, we obtain a linear relationship if we plot $\log\alpha$ vs. the partial charge on the O atoms (Figure 4). The partial charges are calculated by the method of Sanderson [3].

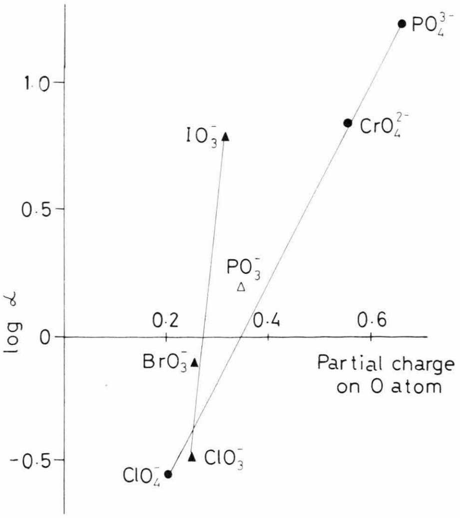

Fig. 4. Plots of $\log\alpha$ of oxoanions vs. partial charge on O atom.

Table 3. R_f values obtained on Merck's plate and $\log\alpha$ calculated.

	R_f*	$\log\alpha$
PO_4^{3-}	0.06	1.29
CrO_4^{2-}	0.16	0.85
ClO_4^-	0.82	−0.56

* Developing solvent c).

In Table 3, values of R_f and $\log\alpha$ calculated for other oxoanions (using the solvent c) are shown. The plots of $\log\alpha$ vs. the partial charge on the O atoms of these anions are also shown in Figure 4. For the XO_4 type anions we obtain a linear relationship, but the correlation factor is not the same as that for XO_3 type anions (halate anions).

In cellulose there exist O radicals, OH radicals and CH_2OH radicals (parts of which are oxidized to COOH radicals and thought to become COO^- in the basic media). So the water fixed on the surface (stationary phase) is thought to be much polarized (Figure 5). The water in the mobile phase can freely move. The inorganic anions are on the one hand hydrated by the water in the mobile phase and on the other hand interact with the water fixed on the surface of the cellulose. The value of $\log\alpha$ is strongly dependent on the ratio stationary/mobile

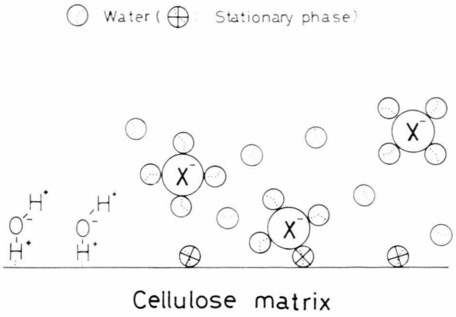

Fig. 5. Schematic figure of anion X⁻ in thin layer chromatography.

water. The interaction with the water fixed on the surface increases with increasing surface charge density on the ion in the case of halide anions (electrostatic attraction). In case of oxoanions the interaction increases with the partial charge on the O atoms (interaction by hydrogen bonds). The number of bonds per molecule is thought to be different for XO_3 and XO_4 type anions, and for this reason the correlations differ. The log α value of the metaphosphate ion is not on the line of the XO_3 type anions in Figure 4. It is thought that this is due to steric hinderance.

Conclusion

i) The volume of the stationary and mobile phases, and the partition coefficient of inorganic anions may be calculated from R_f values obtained by developing these anions simultaneously with mixed metaphosphates.

ii) The volume ratio is very much influenced by the water content of the developing solvent.

iii) The partition coefficients of the halide anions are related to the reciprocal of the ionic radii.

iv) The partition coefficients of oxoanions are related to the partial charge of the O atoms of these anions.

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