N O T E S

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Thin-layer Chromatography of Inorganic Salts. III. Study of the Hydration of Anions by Means of Chromatography of Crystal Violet Cation

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Our object was to obtain information concerning the behavior and the dissolved state of ions in solution by means of chromatography. We suggested that a complex cation is eluted mainly through ion-pair formation with anions contained in a developer.[1] The ion-pair formation reduces the apparent positive charge of a complex cation, which results in the decrease of the electrostatic attraction of an adsorbent and the increase of the R_f value of the complex.

It is well known that a number of anions can be extracted from an aqueous solution into an organic solvent through ion-pair formation between anions and dyestuff cations.[2] The extractability of anions seems to depend largely on the kind of anion and to reflect the behavior of anions towards ion-pair formation. Thus different R_f values of the dyestuff are expected when it is developed with solutions of various salts.

The object of this work is to clarify the effect of hydration of anions on ion-pair formation by means of chromatography of the dyestuff.

Experimental

As an adsorbent, Merck's silica gel H, prepared for thin-layer chromatography was used without further purification. This was spread on glass plates of 20 cm length with 0.25 mm thickness.

The dyestuff used was crystal violet. This was dissolved in ethanol to make 1/1000M solution, and 0.25 μl of the solution was applied at a starting point, 5 cm above the lower edge of the plate.

The following thirteen anions were chosen to form an ion-pair with the crystal violet cation: Cl^-, Br^-, I^-, NO_2^-, NO_3^-, ClO_3^-, ClO_4^-, $CH_3CO_2^-$, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, CO_3^{2-}, SO_3^{2-} and SO_4^{2-}. The sodium salts of these anions were dissolved in 50% ethanol-water solution to make 0.2M solutions, and they were used as a developer (In the case of sulfate and sulfite, 30% ethanol-water solution was used). Development was carried out at room temperature (17—18°C), until the solvent front rose to about 12—13 cm from the starting point. No special procedure was necessary for visualization of the spot, as it was sufficiently colored.

Results and Discussion

In Table 1 are listed the R_f values of crystal violet developed with alcoholic aqueous solutions of various salts, and typical examples of the chromatograms are shown in Fig. 1. As is seen in these data, the R_f value of the dyestuff cation depends

TABLE 1. R_f VALUES OF CRYSTAL VIOLET DEVELOPED WITH ALCOHOLIC AQUEOUS SOLUTIONS OF SALTS

a) Developed with 50% alcoholic aqueous solutions containing monovalent anions in 0.2M

Anions	R_f values	Anions	R_f values
$CH_3CO_2^-$	0.48	ClO_3^-	0.53
$CH_2ClCO_2^-$	0.59	ClO_4^-	0.57
$CHCl_2CO_2^-$	0.63	Cl^-	0.48
NO_2^-	0.44	Br^-	0.52
NO_3^-	0.51	I^-	0.53

b) Developed with 30% alcoholic aqueous solutions containing divalent anions or monovalent anions in 0.1M

Anions	R_f values	anions	R_f values
CO_3^{2-}	0.05	Cl^-	0.14
SO_4^{2-}	0.05	Br^-	0.21
SO_3^{2-}	0.55	I^-	0.22

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1) T. Baba, H. Yoneda and M. Muto, This Bulletin, **41**, 1965 (1968).

2) As examples, the crystal violet-benzene system was used for extraction of ClO_4^- and IO_4^- (C. E. Hedrick and B. A. Berger, *Anal. Chem.*, **38**, 791 (1966)), and for $[Ag(CN)_2]^-$ (J. J. Markham, *Anal. Chem.*, **39**, 241 (1967)). The methylene blue-dichloroethane system was used for extraction of BF_4^- (J. Mrozinski, *Chem. Anal.* (Warsaw), **12**, 93 (1967)).

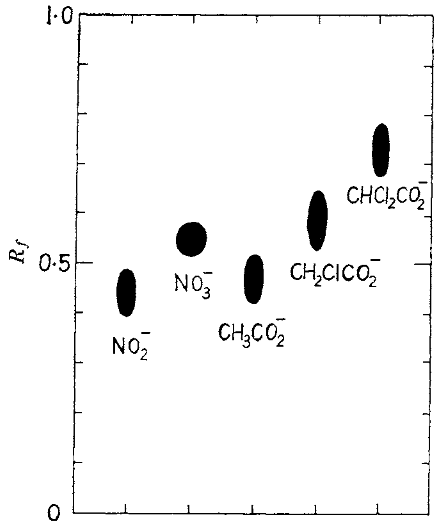
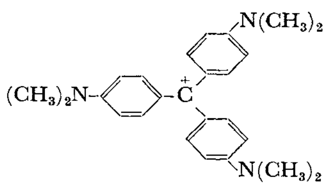


Fig. 1. Chromatogram of crystal violet developed with 50% aqueous alcoholic solutions containing monovalent anions in 0.2M concentration.

on the kind of anion in a developer. Comparison of the R_f values in the pairs ($ClO_4^- > ClO_3^-$ and $NO_3^- > NO_2^-$) and the set ($CHCl_2CO_2^- > CH_2ClCO_2^- > CH_3CO_2^-$) leads us to the following conclusion. The crystal violet cation is dissolved from the adsorbing silica gel surface more easily with a stronger acid anion than with a weaker acid anion. The surface of silica gel is charged negatively in contact with water and adsorbs cations strongly.[4] Thus, the increase of the R_f value of the dyestuff in the salt solution seems to result from the decrease of the apparent positive ionic charge of the dyestuff cation due to the ion-pair formation between the anions and the dyestuff cations. The results suggest that a stronger acid anion can form an ion-pair with a dyestuff cation more easily than a weaker acid anion. As is seen from the structural formula



the crystal violet cation seems to be very poorly hydrated in solution. Presumably a weaker acid anion is more hydrated than a stronger one. Thus we might conclude as follows. The poorly hydrated dyestuff cation can form an ion-pair more easily with the less hydrated anion than with the more hydrated one. In fact, the R_f values of crystal violet increase in the order $Cl^- < Br^- < I^-$. This is just the order of the decrease of hydration. The R_f value in the divalent sulfate and carbonate anions is much lower than that in the monovalent anion. The large R_f value was obtained in the case of the sulfite anion. This can be explained as a result of the reduction of the dyestuff. Thus, the R_f value of the dyestuff is considered to give the relative measure of the degree of hydration of various anions.

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