

CHROM. 5960

Thin-layer chromatographic behavior of a number of transition metals on DEAE-cellulose in azide/chloride media

Metal complexes containing the azide ion have been known for quite some time, but it is only recently that the preparation and properties of azido complexes of the transition metals had been investigated extensively¹⁻⁵. So far, little information is available about ion-exchange behavior of metals in azide media. This prompted us to survey the anion-exchange behavior of the transition metals in these media. Thin-layer chromatographic techniques were used with DEAE-cellulose as the adsorbent in aqueous sodium azide-hydrochloric acid mixtures, as well as in mixed aqueous azide/chloride-organic solvent (methanol) media.

Experimental

About 12 g of DEAE-cellulose (abbreviated now as DEAE), Serva, were treated batchwise by 0.1 *M* sodium hydroxide and washed with deionized water. The DEAE was then converted to the azide form by treating with 0.5 *M* sodium azide solution acidified to a pH of approximately 4.5 with hydrazoic acid which had been prepared using cation-exchange resin in the hydrogen form and finally by washing with deionized water. The DEAE thus prepared was spread 250- μm thick on five sheets of 20 \times 20 cm glass plates. The 250 μm -thick thin-layer plates of DEAE in the chloride form and of microcrystalline cellulose (Avicel SF) were also prepared. All the plates were dried at 40° for 3 h and stored in a desiccator over a saturated potassium bromide solution. Metals⁶ (0.5 μl of 0.1 *M*) were applied to the plate 2 cm from one edge. After drying in the desiccator for 30 min, the plate was developed in a tank previously equilibrated with developing solvent for 1 h. The solvent front was allowed to rise 15 cm from the start. The solvent systems tested were a series of solutions made up by mixing hydrochloric acid and sodium azide solutions of varying concentration to be 0, 0.01, 0.1 or 1 *M* in sodium azide and 0.5 *M* in hydrochloric acid. The pH values were recorded. Mixed solvent systems were binary, consisting of 0.1 *M* sodium azide-0.5 *M* hydrochloric acid solution and methanol in varying proportions. After developing and drying the plate, metals were detected as described previously⁶. The exceptions were Mn(II) and V(IV), which were detected by spraying 0.1 % alkaline 4-(2-pyridylazo)-resorcinol solution, and Ti(IV) which was detected by 0.1 % tannic acid solution.

Results and discussion

In Fig. 1 are illustrated the R_F values for 29 metals on DEAE in the azide form in the aqueous azide-chloride media as a function of azide concentration. For comparison R_F values on DEAE in the chloride form in 0.5 *M* hydrochloric acid are also given. Except for several metals, such as Pd(II), Ag(I), W(VI), Au(III) and Hg(II), most metals do not favor the DEAE phase from the aqueous 0.5 *M* hydrochloric acid. Upon addition of a 0.01 *M* concentration of sodium azide R_F values decrease appreciably for the first transition metals, Y(III), the rare earths, Zr(IV), Nb(V), Mo(VI), Hf(IV), Ir(IV), Pt(IV), Th(IV) and U(VI). For Pd(II), Ag(I), W(VI), Au(III) and Hg(II) the adsorptions are already strong enough, so that the effect of azide is not

evident. Azide seems not to be responsible for the R_F values of Cd(II) and Re(VII).

Hydrazoic acid is a weak acid ($K_a = 2.14 \times 10^{-5}$ at 18°), so that R_F values may be affected by acidity, if the complex formation is responsible for the R_F values involved. R_F values obtained at two pH values are illustrated in Fig. 1 for 1 M azide concentration (pH 3.9 and 1.2). The solution of lower pH was prepared by the addition of perchloric acid. With increasing pH an appreciable lowering of the R_F values is again found for the first transition metals (with exception of Mn(II)), Y(III), the rare earths, Th(IV) and U(VI) and, to a lesser extent, for the metals Zr(IV), Nb(V), Pt(IV), etc.

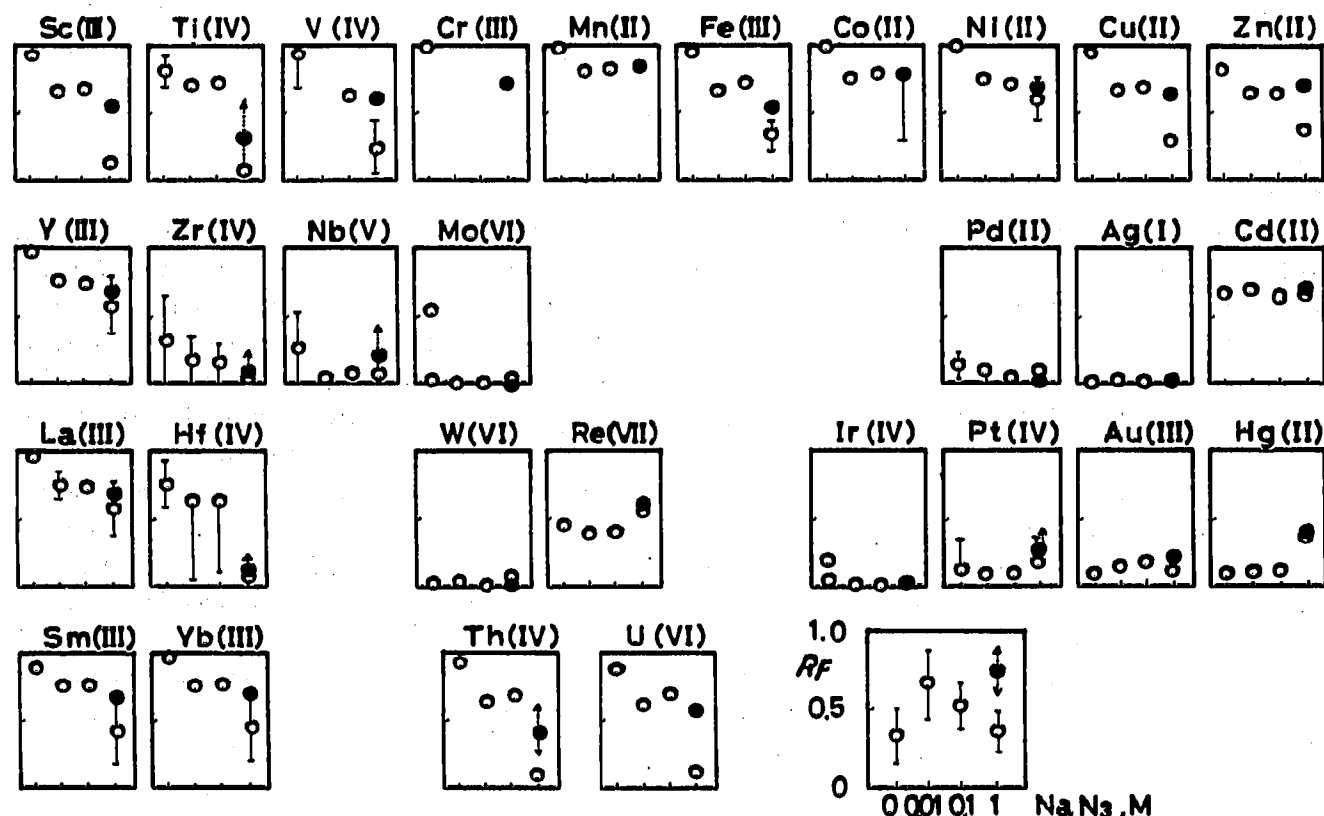


Fig. 1. R_F values of metal ions on DEAE-cellulose in aqueous azide-chloride media as a function of azide concentration. Hydrochloric acid concentration kept constant at 0.5 M. R_F values corresponding to 0 in NaN_3 concentration stand for those on DEAE in the chloride form in 0.5 M HCl; pH: 1.38 for 0.01 M; 1.02 for 0.1 M; 1.17 (●) and 3.90 (○) for 1 M NaN_3 .

In order to observe the effect of chloride concentration R_F values for selected metals were measured as a function of hydrochloric acid concentration. When keeping the azide concentration constant at 0.1 M R_F values for most metals increased with increasing concentration of hydrochloric acid. This was the case even for Pd(II), Ir(IV), Pt(IV), Au(III) and Hg(II). However, R_F values for Mo(VI) and W(VI) remained at zero even if the concentration of hydrochloric acid was increased to 6 M. LEDERER AND OSSICINI⁷ have reported that in the paper chromatography system involving DEAE and hydrochloric acid Mo(VI) exhibited high R_F values (approx. 0.5–0.7) over the hydrochloric acid concentration range of 1 to 8 M. This suggests that the strongest adsorption of Mo(VI) (and perhaps a part of W(VI)) may be caused by azido complex formation.

The formation of metal complexes and subsequent ion-exchange adsorption on DEAE can be facilitated by the addition of a protonic solvent to the aqueous system^{6,8,9}. R_F values were measured for all the metals listed in Fig. 1 in 0.1 *M* sodium azide/0.5 *M* hydrochloric acid-methanol mixtures as a function of methanol concentration (0, 50, 75 and 95% methanol). For the first transition metals, Y(III), the rare earths, Zr(IV), Cd(II), Hf(IV), Re(VII), Th(IV) and U(VI) the adsorption increased linearly with increasing concentration of methanol, the R_F values reaching almost zero at 95% methanol concentration. Strong adsorption ($R_F \sim 0$) was found for Nb(V), Mo(VI), Pd(II), Ag(I), W(VI), Ir(IV), Pt(IV) and Hg(II) over the methanol concentration range tested. Au(III) was the only metal which showed a broad maximum of R_F value around 50-75% methanol.

TABLE I
 R_F VALUES ON DEAE AND AVICEL SF

Metal	0.1 <i>M</i> NaN ₃ -0.5 <i>M</i> HCl	0.1 <i>M</i> NaN ₃ /0.5 <i>M</i> HCl -methanol (1:1)		0.5 <i>M</i> HCl -methanol (1:1)
	Avicel SF	Avicel SF	DEAE ^a	DEAE ^b
Cd(II)	0.87	0.73	0.23	0.22
Cu(II)	0.90	0.81	0.56	0.76
Fe(III)	0.87	0.81	0.58	0.82
Hf(IV)	0.72-0.92	0-0.73	0-0.45	0-0.79
Hg(II)	0.87	0.84	0.05	0.08
Ir(IV)	0.90	0.66-0.87	0.02	0.02
Mo(VI)	0.04, 0.58	0.39	0.01	0, 0.39
Nb(V)	0.63-0.85	0-0.24	0.04	0.05
Re(VII)	0.74	0.79	0.39	0.47
Sc(III)	0.93	0.78	0.43	0.83
Sm(III)	0.92	0.78	0.46	0.82
Th(IV)	0.92	0.59-0.80	0.40	0.79
U(VI)	0.89	0.82	0.45	0.81
V(IV)	0.87	0.89	0-0.55	0.88
W(VI)	0-0.53 ··· 0.99	0-0.48	0.01	0.02
Zr(IV)	0-0.65	0-0.30	0.09	0-0.32

^a Azide form.

^b Chloride form.

··· Weak streak. R_F spread ($R_{F\text{front}} - R_{F\text{rear}}$) being within 0.2, single R_F corresponding to the center of the spread is given.

For the sake of comparison R_F values on a microcrystalline cellulose, Avicel SF, were measured for a selected group of metals in 0.1 *M* sodium azide/0.5 *M* hydrochloric acid-methanol (1:1) as well as in aqueous 0.1 *M* sodium azide-0.5 *M* hydrochloric acid. Results are given in Table I together with R_F values on DEAE in the chloride form in 0.5 *M* hydrochloric acid-methanol (1:1) mixture as reference. As can be seen from Table I, the addition of methanol to the azide-chloride media does not effect the lowering of R_F values on Avicel SF to any significant extent. On the other hand, the addition of methanol allows marked lowering of R_F values on DEAE relative to Avicel SF for all the metals listed. However, comparable increases in adsorption on DEAE in the chloride form from methanolic 0.5 *M* hydrochloric acid are also noticed for Cd(II), Hg(II), Ir(IV), Nb(V), Re(VII) and W(VI). Again, azide seems not to contribute significantly to R_F for Cd(II) and perhaps for Re(VII). Contribution

of azide to R_F for Ir(IV), Nb(V) and W(VI) is not apparent, but may not be excluded. For Hg(II) the effect of azide is not at all clear in this chromatographic study. For the other metals including Cu(II), Fe(III), Hf(IV), Mo(VI), Sc(III), Sm(III), Th(IV) U(VI), V(IV) and Zr(IV), their R_F values on DEAE in the azide form in the mixed solvent medium are low enough compared to R_F values on Avicel SF in the aqueous and mixed solvent media and also to R_F values on DEAE in the chloride form in methanolic 0.5 M hydrochloric acid. The relative lowering of R_F values suggests the easy formation of azido or mixed azido-chloride complexes of these metals and subsequent ion-exchange adsorption on DEAE.

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First received December 20th, 1971, revised manuscript received February 7th, 1972

J. Chromatogr., 69 (1972) 223-226