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Thin-layer Chromatographic Behavior of Transition Metals on a Weakly Basic Cellulosic Ion-Exchanger in Hydrazoic Acid Medium

Rokuro Kuroda and Nobuo Kojima

Laboratory for Analytical Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba

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Metal complexes containing azide ions have received considerable attention recently; the preparation and physical properties of azido complexes of the transition metals have been investigated extensively.[1,2] However, little information is available so far on the ion-exchange behavior of metals in hydrazoic acid media. We have examined the anion-exchange behavior of transition metals in aqueous hydrazoic acid solution. Because of its simplicity and rapidity, the thin-layer chromatographic technique using diethylaminoethylcellulose as an adsorbent was employed to study the adsorbability of metals from the aqueous hydrazioc acid solution.

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[1] L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Spec. Publ. No. 17, Sect. 1, The Chemical Society, London, (1964), p. 160.

[2] For example, R. G. Clem and E. H. Huffman, *J. Inorg. Nucl. Chem.*, **27**, 365 (1965); W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer, and K. Feldl, *Chem. Ber.*, **100**, 2335 (1967); H. -H. Schmidtke and D. Garthoff, *J. Amer. Chem. Soc.*, **89**, 1317 (1967); P. Senise and O. E. S. Godinho, *J. Inorg. Nucl. Chem.*, **32**, 3641 (1970); P. Senise and E. F. de A. Neves, *ibid.*, **33**, 351 (1971); K. Bowman and Z. Dori, *Inorg. Chem.*, **9**, 395 (1970).

Table 1. R_f Values of the transition metals on DEAE-cellulose and avicel SF in 0.1 M HN_3 (pH, 2.8)

Metal	R_f		Metal	R_f	
	DEAE	Avicel SF		DEAE	Avicel SF
Sc(III)	0—0.57	0.79—0.87	Ag(I)	0—0.01	0—0.02
Ti(IV)	0.07—0.12	0—0.91	Cd(II)	0.67—0.77	0.53..0.83—0.87
V(IV)	0—0.54	0.57..0.85—0.89	La(III)	0.72—0.81	0.79—0.89
Cr(III)	0—0.90	0.86—0.94	Sm(III)	0.68—0.79	0.77—0.89
Mn(II)	0.65—0.75	0.69..0.86—0.91	Yb(III)	0.68—0.77	0.81—0.89
Fe(III)	0.08—0.17..0.73	0.83—0.91	Hf(IV)	0.03—0.15	0..0.78—0.86
Co(II)	0.70—0.77	0.50—0.88	W(VI)	0—0.02	0.14—0.71..0.97
Ni(II)	0.70—0.77	0.45—0.87	Re(VII)	0—0.04	0.76—0.87
Cu(II)	0.09—0.13..0.23	0.50—0.83	Ir(IV)	0—0.04	0.84—0.98
			Pt(IV)	0—0.04	0.81—0.97
Zn(II)	0.61—0.72	0.55..0.84—0.89	Au(III)	0—0.03	0.31..0.67—0.73
Y(III)	0.69—0.80	0.81—0.89	Hg(II)	0.03—0.35	0.56—0.66
Zr(IV)	0—0.14	0—0.42	Th(IV)	0—0.39	0..0.76—0.86
Nb(V)	0—0.18	0—0.83			
Mo(VI)	0—0.02	0.15—0.64	U(VI)	0.11—0.29	0.80—0.88
Pd(II)	0—0.02	0—0.70			

"..." Denotes a weak streak.

Experimental

About 12 g of diethylaminoethylcellulose(abbreviated as DEAE), Serva, was treated batchwise by 0.1 M sodium hydroxide and washed with deionized water. DEAE was then converted to the azide form by treating with 0.5 M sodium azide solution acidified with hydrazoic acid to pH 5. In order to obtain hydrazoic acid, a 0.5 M sodium azide solution was passed through a column of cation-exchange resin in the hydrogen form. After washing with deionized water by centrifugation, DEAE was slurried with 35 m*l* of deionized water and spread 250 μ thick on five 20×20 cm glass plates. The 250 μ thick thin-layer plates of microcrystalline cellulose, Avicel SF(Avicel Sales Division, FMC Corp.), were also prepared.[3] All the plates were dried at 40°C for 3 hr and stored in a desiccator containing a saturated potassium bromide solution. For most metals the test solutions were 0.1 M metal chlorides of varying hydrochloric acid concentration. The test solutions of Nb(V), Mo(VI), Ag(I), W(VI), and Re(VII) were prepared as reported previously.[3]

A 0.5 μl portion of the test solutions was applied to the plate at 2 cm from the edge. After drying the plate in the desiccator for 30 min, it was developed in a tank(23×11×22 cm) equilibrated with 0.1 M hydrazoic acid solution for 1 hr. After developing (solvent front 15 cm high) and drying the plate, metals were detected.[3] Mn(II) and V(IV) were detected by spraying 0.1% alkaline PAR solution, and Ti(IV) by 0.1% tannic acid solution.

Results and Discussion

In Table 1 the R_f values are given for 29 metals on DEAE together with those on a plain cellulose Avicel SF as a reference, both in 0.10 M hydrazoic acid solution. We see that almost none of the metals are adsorbed on Avicel SF from 0.1 M hydrazoic acid. Ag(I) forms an insoluble precipitate with azide, giving the R_f value of approximately zero. In contrast to Avicel SF, enhanced adsorption can be observed for most metals on DEAE in hydrazoic acid solution. Within the group of the first transition metals, Mn(II), Co(II), Ni(II), and Zn(II) are not adsorbed on DEAE while the other metals including Sc(III), Ti(IV), V(IV), Cr(III), Fe(III), and Cu(II) exhibited increased adsorption on DEAE relative to Avicel SF, although marked streaks were often found for some of them.

It is of interest to note that the hydrazoic acid allows the strongest adsorption on DEAE of Mo(VI), W(VI), Re(VII), and the platinum group of metals including Pd(II), Ir(IV), and Pt(IV). All the metals except for Ir(IV) have been reported to be adsorbed strongly on DEAE from thiocyanic acid,[4,5] which resembles hydrazoic acid in many aspects, both being grouped to pseudohalogenic acid.

Considerable differences in the adsorbability between DEAE and Avicel SF are also observed for Zr(IV), Nb(V), Hf(IV), Au(III), Hg(II), Th(IV), and U(VI). This is also the case for Y(III) and the rare earth metals, the difference being less remarkable. Cd(II) behaves like Zn(II). Diethylaminoethyl group does not seem to be responsible for the R_f value of Cd(II) on DEAE, even though a weak azido complex formation takes place.[6] The R_f value is rather high for Hg(II).

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[3] K. Oguma and R. Kuroda, *J. Chromatogr.*, **52**, 339 (1970).

[4] K. Ishida and R. Kuroda, *Anal. Chem.*, **39**, 212 (1967).

[5] K. Ishida, T. Kiriyama, and R. Kuroda, *Anal. Chim. Acta*, **41**, 537 (1968).

[6] P. Senise and E. F. de A. Neves, *J. Amer. Chem. Soc.*, **83**, 4146 (1961).

This might not allow the uptake of Hg(II) on a DEAE column from 0.1 M hydrazoic acid. This is in contrast to its behavior in thiocyanate media, where the pronouced adsorption of Hg(II) takes place, permitting a very specific column separation of Hg(II) from about 40 metals.⁷⁾

The absorption of the transition metals on DEAE from the hydrazoic acid solution may be mostly accounted for, by assuming azido complex formation and the subsequent anion-exchange. However, it might be possible for some metals that adsorption is caused merely through the anion-exchange of their oxyanions.

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7) R. Kuroda, T. Kiriyama, and K. Ishida, *Anal. Chim. Acta*, **40**, 305 (1968).