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## EFFECT OF NITRITE MEDIA ON $K_D$ VALUES IN AQUEOUS AND AQUEOUS-METHANOLIC SOLUTION FOR CATION AND ANION EXCHANGERS

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The distribution coefficients of a group of metal ions has been determined in nitrite media, with cation as well as anion exchangers. Sodium nitrite solution has been used as a complexing agent for these metal ions, giving anionic complexes in aqueous solution. The same studies have been performed in aqueous methanol. Changing the proportion of methanol has a marked influence on complex formation and consequently on the  $K_D$  values.

### INTRODUCTION

Distribution studies in chloride, sulphate and nitrite media in aqueous solutions for both cation and anion exchangers have been reported previously [1,2]. Addition of polar organic solvents to water solutions modifies the affinities, thus producing a condition that is widely different from that in the absence of solvent [3]. The separation of cadmium(II) from zinc(II), manganese(II), cobalt(II), nickel(II) and bismuth(III) has been effected by ion exchange chromatography over Amberlite IR-120 using nitrite as eluting agent. Sodium nitrite, 2%, elutes only cadmium(II). Zinc(II), manganese(II), cobalt(II) and nickel(II) are then eluted by 5-10% sodium nitrite solution leaving bismuth alone in the column [5].

Ion exchange distribution of some metal ions has been studied in nitrite media, with cation as well as anion exchangers. Similar studies have been carried out in aqueous ethanol. Increasing the concentration of ethanol leads to increased complex formation and changes  $K_D$  values [4]. Sodium nitrite solution has been used as complexing agent in the cation exchange chromatographic separation of Pb(II) in binary and ternary combinations with Ti(I), Cd(II) and Bi(III) [6].

A method for the simple and rapid separation of small quantities of nickel from both cobalt and manganese has been described. By using a medium consisting of 9N HCl solution, a mixture of the three elements is added to a small column of strongly-basic anion exchange Amberlite IRA-400. For the elution of cobalt and manganese, 6 N. NHCl solution is employed [7]. This method can be used for the separation of copper, iron and zinc from one

another [8].

In the present paper the cation and anion-exchange characteristics of 6 elements towards the strongly acidic as well as basic exchangers in media containing varying concentrations of methanol and aqueous nitrite are presented. Based on the determination of the distribution coefficients of these elements in aqueous as well as aqueous methanolic solutions, the conditions most suitable for their separation are indicated and discussed.

### EXPERIMENTAL

*Reagents.* Air-dried strongly acid macroreticular cation exchanger (Amberlite 252, Na-form; Cap. 2.9 meq/g), and anion exchangers (Amberlite IRA-400, NO<sub>2</sub>-form; Cap. 4.4 meq/g) 100-200 mesh. (Analytical reagent quality, Rohm & Haas Co. Philadelphia, Pa).

The salt solutions used were prepared from their nitrites to give 0.1N solution in aqueous and aqueous methanolic media. Absolute methanol; and British Drug House Analar quality sodium nitrite were used.

The concentrations of Co(II), Ni(II), Cu(II) and Pb(II) were determined titrimetrically with EDTA, while Ag(I) and Hg(II) were titrated with ammonium thiocyanate, in presence of nitric acid solution, and with iron(III) as indicator.

*Determination of the  $K_D$ .* The distribution studies were carried out in a glass stoppered flask (250 ml) containing 1 g. of the resin and 50 ml of the metal ion solution (0.1N) in aqueous nitrite medium. Batches were equilibrated by shaking for 24 hrs. All the experiments were carried out at room temperature (30°). Each solu-

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tion was analysed for the metal ion. The weight distribution coefficient ( $K_D$ ) values were calculated from the relation[4].

$$K_D = \frac{\text{meq. metal/g. of dry resin}}{\text{meq. metal/ml. of solution}}$$

It should be noted that the distribution coefficients of both silver and mercury in methanolic nitrite media could not be determined because of the insolubility of the compound formed.

### RESULTS AND DISCUSSION

The distribution data in Table (1) for the cation exchange resin Amberlite 252 indicate that  $K_D$  decreases gradually with nitrite concentration for lead, cobalt and nickel but not for copper(II), and mercury(II). It is probable that the increase in the formed nitrite complexes with lead, cobalt and nickel ions due to the higher concentration of sodium nitrite, results in a decrease in the amount of exchanged metal ions by the resin, (a decrease in  $K_D$  values). At 0.3, 0.5, 0.7 and 1.0N. nitrite, the  $K_D$  value for mercury is zero, indicating that such complex did not exchange. It seems therefore, that mercury forms a stable complex with the nitrite at these concentration; mercury can thus be easily separated from other ions such as Co(II) and Ni(II).

At 0.1N nitrite; copper(II) has the lowest  $K_D$  values and consequently can be readily separated from these ions. The cation exchange distribution values obtained agreed well with those previously reported, using sodium nitrite as complexing agent[4].

A possible separation of copper(II) from other metals can be obtained at nitrite concentration of both 1.0 and 1.5N. where copper exhibits the highest  $K_D$  values.

Most of the results accord well with those reported by Bhatnagar in his study on cation exchange separations using sodium nitrite as eluent[5,7].

Distribution data for anion exchange studies are given in Table (2). It is clearly evident, that the ions, not sorbed by cation exchangers in nitrite media, are strongly sorbed by anion exchanger, IRA-400. Metals anionic complexes with nitrite ions gave high distribution values and consequently are strongly sorbed. The  $K_D$  values in Table (2) can be used to indicate possible exchange separation for cobalt, nickel and lead from silver, mercury and copper by converting ionic species into the anionic complex by adding sodium nitrite of suitable concentration, and then allowed to pass over anion exchange resin. The anionic

complex taken up by the resin can be eluted with another reagent having no complexing property. Such similar results was reported by Bhatnagar[4] in the presence of Dowex-1X8 anion exchanger.

Distribution studies in aqueous methanolic solutions containing various concentrations of nitrite, showed general decrease in  $K_D$  with increasing the normalities of nitrite for cobalt, nickel, copper and lead (c.f. Table 1). The tabulated results indicate that Ni ion showed enhanced complex formation in presence of methanol, thus preventing the sorption of the complexed metal ion by the cation exchanger. The effect of increasing the proportion of alcohol is clearly observed when  $K_D$  values for lead, copper and cobalt ions are compared for the three solvent compositions. The distribution values increased with the increase in the percentage of alcohol, showing that the addition of polar organic solvents to water solution at low concentration of the eluent agent, modifies the selectivities further in a number of cases and thus leads to conditions which are otherwise unattainable in aqueous solution. A review on this subject has been published by Korkish[12]. Ag(I) and Hg(II) in methanolic nitrite media could not be determined because an insoluble matter was formed on the resin. Upon increasing the proportion of alcohol at higher concentration of nitrite solution i.e., 1.5 and 2.0N for the three solvent concentrations, the distribution values decreased by increasing the percentage of alcohol, showing enhanced complex formation, which may be attributed to the addition of solvent of dielectric constant lower than that of water. These observations agree well with those made by Bhatnagar[4]. From these results it can be stated that, in the presence of 40% V/V methanol and 0.05 N. nitrite concentration, cobalt ion can be eluted from other ions; whereas lead and nickel ions at 40 and 50% V/V methanol and 0.7 to 2.0N nitrite solution can be separated from copper(II).

The studies on anion exchanger with alcoholic solution (Table 2) showed an increase in exchange with increasing nitrite concentrations. The ions which form stable complexes exchanged more readily because the complexes formed were anionic species. Copper and silver ions have higher  $K_D$  values than those given by cobalt and nickel. From Table (2) it is evident that in nitrite concentration in the range of 0.05 – 0.2N and 50% aqueous methanol, copper can be readily separated from lead. In the presence of 0.2 N nitrite concentration and 49% methanol copper-nickel separation is also possible.

Bhatnagar and his associates have reported that silver, mercury and copper formed much stronger anionic nitrite complexes[5,9,10]. Investigations made by Hagemuller[11]



Table 1.  $K_D$  values in aqueous and aqueous-methanolic nitrite on cation exchanger

Ion	A-pure aqueous media							
	Nitrite concentration (N)							
	0.1	0.3	0.5	0.7	1.0	1.5	2.0	3.0
Ag(I)	30	21	19	8	8	8	8	8
Hg(II)	38	0	0	00	7	7	7	14
Pb(II)	57	30	14	7	4	2	2	2
Cu(II)	10	57	53	29	48	44	41	47
Co(II)	64	32	18	13	10	5	5	5
Ni(II)	59	30	23	10	8	9	10	5

  

Ion	B-30% (V/V) methanol							
	Nitrite Concentration (N)							
	0.5	1.0	0.3	0.5	0.7	1.0	1.5	2.5
Ag(I)	ppt.	ppt.	ppt.	pp.t	ppt.	ppt.	ppt.	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	15	25	24	8	9	8	8	8
Cu(II)	125	123	128	90	77	64	57	56
Co(II)	75	50	23	10	0	0	0	0
Ni(II)	42	30	25	7	5	5	5	5

  

C-40% (V/V) methanol								
Ag(I)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	32	46	0	0	0	0	0	0
Cu(II)	135	124	125	94	77	72	71	55
Co(II)	268	122	42	21	23	19	18	17
Ni(II)	40	28	12	7	0	0	0	0

  

50% methanol (V/V)								
Ag(I)	ppt.	ppt.	ppt.	ppt	ppt.	ppt.	ppt	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	75	20	0	0	00	0	0	0
Cu(II)	163	143	135	147	142	81	43	40
Co(II)	104	84	41	17	11	7	5	5
Ni(II)	32	25	13	7	0	0	0	0



Table 2.  $K_D$  values in aqueous and aqueous methanol nitrite on anion exchanger.

Ion	A-pure aqueous media							
	Nitrite concentration(N)							
	0.1	0.3	0.5	0.7	1.0	1.5	2.0	3.0
Ag(I)	12	65	55	25	40	30	54	40
Hg(II)	36	210	150	133	112	98	82	80
Pb(II)	10	50	43	30	29	28	30	30
Cu(II)	30	35	54	50	20	56	40	35
Co(II)	7	10	12	20	25	38	40	70
Ni(II)	0	0	0	0	5	13	32	30
	B-30% (V/V) methanol							
	Nitrite concentration (N)							
	0.05	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	43	16	0.0	0.0	0.0	0.0	0.0	0.0
Cu(II)	19	35	90	95	92	100	142	102
Co(II)	0.0	0.0	0.0	13	18	35	42	23
Ni(II)	0.0	0.0	0.0	14	8	6	15	13
	C-40% (V/V) methanol							
	0.05	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	0.0	0.0	0.0	0.0	7	0.0	0.0	0.0
Cu(II)	33	41	123	192	190	193	190	192
Co(II)	5	6	5	32	34	59	71	82
Ni(II)	0.0	0.0	0.0	6	10	7	18	20
	D-60% (V/V) methanol							
	0.05	0.1	0.3	0.5	0.7	1.0	1.5	2.0
Ag(I)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Hg(II)	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.	ppt.
Pb(II)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu(II)	53	120	120	190	102	107	107	103
Co(II)	17	15	16	46	67	98	60	61
Ni(II)	0.0	0.0	0.0	9	22	28	37	35

have confirmed the formation of two types of anionic lead complexes with nitrite. Much weaker anionic nitrite complexes[5] are being formed with cobalt and nickel ions. There is a fair agreement between the distribution data reported by other workers for these metal ions and the investigations reported here.

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