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**SPECTROPHOTOMETRIC STUDIES TO DETERMINE THE DISTRIBUTION COEFFICIENT OF SOME METAL IONS ON ANION EXCHANGE RESIN IN PRESENCE OF E.B.T. DYE.**

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**Abstract**

The absorption spectra of various concentrations of some metal nitrate salts; Co(II), Ni(II), Cu(II) and Cr(III) nitrate, with different concentrations of Eriochrome Black T (E.B.T) dye solutions were studied in the presence and absence of Dowex – S.B.R. anion exchange resin ( nitrate form ) . The calculated values of distribution coefficient  $k_d$  illustrate the importance of the E.B.T dye solution as complexing agent for the removal of different metal ions on the Dowex – S.B.R. anion exchange resin. The same studies have been performed for samples in different molarities of nitric acid at constant concentration of E.B.T. and metal ion solution for only Co ( II ) and Ni ( II ) ions since Cu ( II ) and Cr ( III ) ions precipitate in the presence of E.B.T. The nitric acid imported also a marked influence on Co and Ni ions complex formation and consequently on their  $k_d$  values. Ethanol and acetone were used in different proportions to evaluate the effect of changing the dielectric constant of the medium on the  $k_d$  values of the Co and Ni with E.B.T. in the studied solutions. The  $k_d$  values are markedly higher in acetone – dye – metal ion - water media as compared with those obtained in aqueous – ethanol – dye – metal ion mixture at the same concentrations. The effects of pH on the absorption and  $k_d$  behavior for Co (II) and Ni (II) ions in presence of E.B.T. dye on the Dowex – S.B.R. anion exchange resin were studied and discussed.

**Introduction**

Several attempts have been carried out using spectrophotometric methods to explore the stoichiometry of the reaction of alizarin or alizarin S with zirconium and hafnium in aqueous or alcohol solution ( 1-5 ) . Katzin and Gebert ( 6 ) studied the behavior of lithium chloride , lithium nitrate , cobalt chloride and nickel nitrate on the chloride and nitrate form of the anion exchange resins from acetone solution . They noted that the whole salts were adsorbed as complex anions. The adsorption of uranium on strongly basic resins from nitric acid solutions have been studied in detail by several workers (7-10). Aromatic complexing agents containing sulphonic groups are particularly useful in the separation of metal ions on anion exchange resin<sup>(11)</sup>. Chelating groups have been introduced into resin via synthetic technique or

by simple loading, and the modified resins have been used for the selective recovery or preconcentration of metal ions <sup>(12)</sup>.

Many enrichment procedures as liquid – liquid extraction, co precipitation and also several systems of adsorption and sorbents such as polymeric resins, activated carbon, silica and others have been reported in the literature <sup>(13-18)</sup>.

Eriochrome Black T (E.B.T) has been widely used as a chromatographic agent in the determination of metal ions by complexometric titration or spectrophotometric method <sup>(19)</sup>. Many complexing agents, which form negatively charged complexes, have been employed for the separation of metal ions on ion exchange resin. The separations are based on the different stabilities of the complexes and their affinities for the resin <sup>(20)</sup>. Ion exchange distribution of Eriochrome Black T, Xylenol orange and Rhodamine B dyes with strong anion exchange resin has been investigated in aqueous media <sup>(21)</sup>.

The present work aims at the determination and evolution of distribution coefficients for some divalent and trivalent metal ions measured in combination with Eriochrome Black T by Dowex – S.B.R. anion exchange resin. The effect of nitric acid, the addition of some organic solvents and solutions of different pH values were also studied in water media.

## **Experimental:**

### *Material:*

Dowex S.B.R. anion exchange resin (Cl<sup>-</sup> form) from BDH with exchange capacity of 3.488 m equi / g dry resin was used. The used other materials were delivered as follows, [(cobalt, nickel, copper and chrome nitrate) from Fluka, (Eriochrome Black T) from Sigma, (nitric acid , ethanol and acetone) from BDH].

### *Apparatus:*

Double beam UV visible spectrophotometer Jasco V - 570 UV / VIS / NIR with wave length range between ( 300 - 800 ) nm was used to determine the concentrations of the different ions in the studied solutions .

### *Preparation of solutions:*

Stock nitrate solutions of Co (II) , Ni (II) , Cu (II) and Cr (III) in aqueous media

having the respective concentrations of ( 0.6 , 0.6 , 0.2 and 0.3 M ) respectively were prepared . A stock solution of EBT  $2.16 \times 10^{-4}$  M was prepared also in water. Stock solutions were used then to prepare different dilute concentrations. Nitric acid solutions of different concentrations (0.1, 0.3, 0.5, 0.7, 0.9 M) were also prepared. The equilibrium concentrations of metal ions and EBT dye in the different solutions were determined spectrophotometrically.

The distribution coefficient  $K_d$  for each ion was calculated according to the following relation<sup>(22)</sup>:

$$K_d = \frac{\text{amount of metal ion per gram of dry resin}}{\text{amount of metal on per ml of solution}}$$

### Results and discussion:

Anion exchange studies have been carried out for Co (II) , Ni (II) , Cu (II) and Cr (III) using their nitrate salt aqueous solutions . The obtained zero order  $K_d$  values for the different ions indicate that their isn't any indication of metal complex ion formation in the studied concentration in aqueous media, Table (1).

Results of the dependence of Co (II) , Ni (II) , Cu (II) and Cr (III) ion retention on Dowex S.B.R. in presence of EBT dye at different metal : EBT solutions ratios are given in Table ( 2 ) . It is clear from the results that , the distribution coefficient for Co (II) and Ni (II) shows rise in their values with changing in their molar volume ratios( M : EBT ) from ( 18 : 2 ) to ( 2 : 18 ) ;. From the obtained results, two mechanisms can be suggested. The first one is that Dowex S.B.R. sorbed the Eriochrome Blake T and then the Co (II) and Ni (II) ions were exchanged on the sorbed EBT dye. The second probable suggested mechanism is that the EBT dye interacted with the two ions in the aqueous solutions and forms the dye metal ion complex which can be then adsorbed on the used anion exchange resin. The suggestion of dye metal ion complex formation can be enhanced by the obtained precipitation of Cu (II) and Cr (III) ions with EBT dye ions in aqueous solutions.

The sorption behavior of metal ions on EBT dye of resin as a function of metal ion concentrations reveals many interesting features; the Co (II) and Ni (II) ions were strongly adsorbed with the dye by the anion exchanger. This is due to the fact that the exchange resin incorporates chelating agent by the  $\pi$  bond because of the interaction between the benzene ring of EBT dye and the divinyl benzene of the resin matrix, which in turn reacts with the metal ions to form metal chelates having

different values of stability constants. The stronger the formed dye chelates, the stronger the hold of the metal ion by the resin<sup>(23)</sup>.

Generally, EBT dye displays high affinity for anion exchange in order to enhance the selectivity of such dye resins materials towards metal ions. These results agree well with the results of several researchers<sup>(24, 25)</sup>.

The effect of nitric acid concentrations ( 0.1-0.9 M ) on the anion exchange characteristics of Co (II) and Ni (II) towards the strongly basic anion exchange resin; Dowex S.B.R. in the presence of constant molar volume ratio of EBT dye relative to those of metal ion solutions have been investigated and the obtained results are given in Table ( 3 ). The resulted  $K_d$  values indicated that the nitric acid affected the removal of Co (II) and Ni (II) ions from the solution. This behavior is due to the formation of an ionic complex<sup>(25)</sup>. Co (II) and Ni (II) show maximum adsorption values in 0.5 M nitric acid. This behavior is mentioned to be expected<sup>(26)</sup> when nitrate ions enter into the complex form. However, the reduced adsorption at the other concentrations of  $\text{HNO}_3$  could be due to the presence of EBT dye in the solution which may reduce the affinity of the metal nitrate complex towards the anion exchanger where competition between the two complexing agents in the solution occurs to form complexes with the metal ions on the resin. On the other hand the acid media have pronounced effect on the dissociation of the dye ion<sup>(27)</sup>.

The effects of dielectric constant (DC) on the adsorption behavior of Co (II) and Ni (II) ions on the anionic resin were studied by the addition of different percentages of ethanol and acetone to the dye with the metal ion solution.

The effect of (DC) on adsorption was earlier observed by Sakaki and Kakihana<sup>(28)</sup> in equilibrium experiments with K, Na and Li ions in organic solvents media. The influence of increasing proportion of ethanol and acetone on the distribution coefficient values of metal ions are given in Table (4). The  $K_d$  values of Co (II) reach maximum value at 30 % V/V of both organic solvents as compared with the pure water or in mixture containing 10 or 50 % V/V organic solvent. The  $K_d$  values for Ni (II) are higher than those in case of Co ( II ) ions in the same organic solvent percentage, also its values increased by increasing the organic solvent percentage. This means that in such solution the free metal ions which exist and can react with the dye to form complexes and consequently the  $K_d$  values affected by the dielectric constant of the media<sup>(29)</sup>.

Table ( 5 ) illustrates the pH dependence of the exchange capacity for the E.B.T dye from the resin ; the maximum is observed in the pure water and  $K_d$  values for Co (II) and Ni (II) were decreased by raising the pH value of the exchange media . The noticed reduction at the different pH values may be due to the change in the E.B.T species, and precipitation takes place for Ni (II) at some buffer solutions.

**Table ( 1 ) : The distribution coefficient ( $K_d$ ) for different concentrations of Co (II), Ni (II), Cu (II) and Cr (III) Ions on Dowex-S.B.R. in aqueous solutions.**

<i>Metal Ions</i>	<i>Metal Ion Concentrations(M)</i>	<i>Distribution Coefficient (<math>K_d</math>)</i>	<i>Metal Ions</i>	<i>Metal Ion Concentrations(M)</i>	<i>Distribution Coefficient (<math>K_d</math>)</i>
<i>Co (II)</i>	0.360	0.00	<i>Cu (II)</i>	0.072	0.00
	0.320	0.00		0.064	0.00
	0.280	0.00		0.056	0.00
	0.240	0.00		0.048	0.00
	0.200	0.00		0.040	0.00
	0.160	0.00		0.032	0.00
	0.120	0.00		0.024	0.00
	0.080	0.00		0.016	0.00
	0.040	0.00		0.008	0.00
<i>Ni (II)</i>	0.360	0.00	<i>Cr (III)</i>	0.144	0.00
	0.320	0.00		0.128	0.00
	0.280	0.00		0.112	0.00
	0.240	0.00		0.096	0.00
	0.200	0.00		0.080	0.00
	0.160	0.00		0.064	0.00
	0.120	0.00		0.048	0.00
	0.080	0.00		0.032	0.00
	0.040	0.00		0.016	0.00

**Table (2): The Distributions coefficient ( $K_d$ ) for Co (II), Ni (II), Cu (II) and Cr (III) ions on Doewx- S.B.R. in presence of E.B.T dye at different metal: E.B.T solutions ratios.**

<i>Metal to Dye Volume M : E.B.T</i>	<i>Co (II)</i>		<i>Ni (II)</i>		<i>Cu (II)</i>		<i>Cr (III)</i>	
	<i>Metal Conc. (M)</i>	$K_d$	<i>Metal Conc. (M)</i>	$K_d$	<i>Metal Conc. (M)</i>	$K_d$	<i>Metal Conc. (M)</i>	$K_d$
18 : 2	0.360	2.08	0.360	1.43	0.072	ppt.	0.144	ppt.
16 : 4	0.320	3.24	0.320	2.81	0.064	ppt.	0.128	ppt.
14 : 6	0.280	5.03	0.280	3.96	0.056	ppt.	0.112	ppt.
12 : 8	0.240	6.10	0.240	4.37	0.048	ppt.	0.096	ppt.
10 : 10	0.200	9.59	0.200	5.52	0.040	ppt.	0.080	ppt.
08 : 12	0.160	11.16	0.160	9.08	0.032	ppt.	0.064	ppt.
06 : 14	0.120	12.37	0.120	15.86	0.024	ppt.	0.048	ppt.
04 : 16	0.080	16.67	0.080	23.66	0.016	ppt.	0.032	ppt.
02 : 18	0.040	21.68	0.040	40.09	0.008	ppt.	0.016	ppt.

**Table (3): The distribution coefficient ( $K_d$ ) for different concentrations of Co (II) and Ni (II) ions on Dowex-S.B.R. in the presence of (2:18) ratio of metal : E.B.T dye solution and different  $HNO_3$  concentrations.**

<b>Metal Ion</b>	<i>HNO<sub>3</sub> Concentration (M)</i>					
	<i>K<sub>d</sub> values</i>					
	Pure Water	0.1	0.3	0.5	0.7	0.9
<i>Co (II)</i>	21.68	26.63	13.09	52.04	3.05	7.64
<i>Ni (II)</i>	40.09	37.72	61.11	74.22	56.95	60.50

**Table (4): The distribution coefficient ( $K_d$ ) for different concentrations of Co (II) and Ni (II) ions on Dowex-S.B.R. in presence of (2:18) metal : E.B.T dye solution ratio and different proportions of ethanol and acetone.**

<i>Metal Ion</i>	<i>Percentage of Organic Solvent (V/V)</i>						
	<i>Pure Water</i>	<i>Ethanol</i>			<i>Acetone</i>		
		10%	30%	50%	10%	30%	50%
<i>Co (II)</i>	21.68	20.42	25.76	23.53	34.03	46.15	41.32
<i>Ni (II)</i>	40.09	26.05	36.21	48.04	40.09	42.59	67.65

**Table (5): The distribution coefficient ( $K_d$ ) for different concentrations of Co ( II ) and Ni ( II ) ions on Dowex-S.B.R. in presence of (2:18) metal : E.B.T dye solution ratio and different pH values of the exchange media.**

<i>pH values</i>	<i>Metal ion</i>			
	<i>Co(II)</i>		<i>Ni(II)</i>	
	$K_d$	$\log K_d$	$K_d$	$\log K_d$
<i>Pure water</i>	21.68	1.34	40.09	1.60
<i>2.801</i>	15.15	1.18	30.00	1.48
<i>4.054</i>	13.69	1.14	ppt.	–
<i>4.989</i>	12.31	1.09	ppt.	–
<i>9.376</i>	11.54	1.06	14.93	1.17

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