CATION EXCHANGE DISTRIBUTION BEHAVIOR OF SOME ELEMENTS IN AMMONIUM SULFAMATE-AQUEOUS-DIOXAN MEDIA ON TULSION T – 42H ORGANIC CATION EXCHANGER

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Abstract

Ion Exchange distribution coefficient K_d-values have been measured for the partition of some metal ions, between Tulsion T–42 NH_4 - form and a media which contain organic - aqueous - Sulfamate systems. A decreasing behavior of the distribution coefficients with the increase of sulfamate solution has been observed. The influence of change of the dielectric constant (DC) of the sorption medium has been also evaluated by using 10%, 20%, 30% and 40% (v/v) of the dioxan solution. Based on the calculated K_d - values obtained from the experimental data, several useful separations have been suggested and investigated for some binary systems under study.

Introduction:

A survey of the available literature indicates that a number of complex agents have been used for the separation of some metal ions at different kinds of ion exchanges (1 - 5). It shows that the addition of organic solvent to water medium leads to the modification of the affinities of metal ions towards ion exchangers, thus giving conditions that are widely different from that in the absence of solvent. Moreover, It was found that in some cases, the distribution coefficient value of metal ions may increase or decrease in the presence of organic solvents.

Glycine and other amino - acids along with other complexants were used as retarding agents, for the separation of several less familiar elements in the exchange resin of NH_4^+ - form and of some metal ions in binary systems (6). Glycine hydroximate on divinyl benzene styrene copolymer shows a different variation in the adsorption of some metal ions in the presence of varying range of pH's of the medium (5). Thiourea (7) and others such as "other buffer solution" (8) in the range from (1-6), along with complexants, have been also investigated as retarding agents for the separation of several elements. Sulfamate, as a base of moderately strong acid, has been investigated from many years (9). We should mention that there is no knowledge obtained from the study of the ion exchanger behavior in sulfamate media, except only in the case of 40% (v/v) ethanol (10) and 40% (v/v) acetone (11).

The purpose of the present work is to explore the possibilities of separation of some toxic elements from the solution such as Hg(II), Cd(II) and Pb(II) ions and

from matrices by using a Tulsion T - 42 (NH_4^+ - form) chelating resin. The adsorption behavior of Mg(II), Ni(II), Fe(III), Zn(II), Cd(II), Cu(II), Pb(II), Hg(II) and Th(IV) ions in the resin were investigated at different properties of dioxan 10%, 20%, 30% and 40% (v/v) solution. The separation is based on the affinity differences of these ions towards the chelating resin as a function of ammonium sulfamate concentrations.

This paper describes the systematic investigation of column separation and pre-concentration of Hg(II) or Pb(II) and / or Pb(II) as their sulfamate from the solution in a strong acid cation exchange resin hydrogen cycle Tulsion T -42H chelating resin in a column, based on the distribution data Hg(II) or others in binary system with higher retained other metal ions a separation has been investigated.

Experimental method:

Reagents and materials.

Strong acid cation exchange resin - hydrogen cycle Tulsion T -42, provided from Water Projects Saudi Arabia Ltd., was converted into the NH_4^+ form by treating it with ammonium buffer 1 mole/ 1-5% ammonium chloride solution. The resin has been washed with ethyl alcohol, until Cl^- ions was removed against $AgNO_3$ solution. Next, the resin has been air dried by suction on sintered bed. Both of (250-420 mesh size) using test sives and ASTM-E 11-61 have been used in this investigation and provided from Bayer AG Company. The exchange capacity 2.43 meq/ml[12], moisture content 52% in H^+ - form and 47% in NH_4 form. The chemical structure: Polystyrene divinyl benzene-SO_3H.

The stock solutions of Mg(II), Ni(II), Fe(II), Zn(II), Cd(II), Cu(II), Pb(II) and Th(IV) ions have been prepared by the dissolution of their nitrates in aqueous as well as in aqueous - dioxan media (if desired, a small amount of HNO_3 or HCl was added to stop the hydrolysis) and standardized against EDTA. Ammonium sulfamate Loba, Germany was used for preparation of solutions (0.01 - 2.0 M).

The concentration of metal cations was determined by titration with EDTA - disodium salt as titrant employing muroxide, Eirochrem Black- T, methyl thymol blue, xylenol orange, hexamine and sulphosalicylic acid as indicator. HNO_3 solution has also been used in some cases [12,13].

Determination of K_d : The distribution study was carried out in a 100 ml glass - stoppered flak containing the dry resin (1 g) in NH_4^+ form in aqueous and aqueous - dioxan media. Calculation of the distribution studies was done by shaking the flasks for 8 hr. All experiments were carried out at 25 ± 0.1°C. The exchange resin was

filtered off and remained metal ion content that was left in the liquid phase and determined by EDTA. disodium salt solution O.OIM. The distribution values (K_d) were calculated by the following equation (5).

$$K_d = \frac{m \text{ equiv. metal/ 1 g dry resin}}{m \text{ equiv. metal / ml of solution}}$$

Separation method:

A slurry of exact 6.0 g of a dried resin in NH_4^+ - form was packed into a burrette and has (1,2 cm) internal diameter with the help of glass wool support and tap. The burrette was filled by the passage of the desired concentration of NH2 S03 NH4 and then added binary system of the investigated metal ions in ammonium sulfamate solution 10 ml 2 mg was powered into the column at a flow rate of 2 - 3 ml / min, followed by 100ml of redistilled water (1).

Results and Discussion

The molar distribution coefficient values were determined for some di - , tri - and tetravalent metal ions such as; Mg(II), Ni(II), Fe(III), Zn(II), Cd(II), Cu(II), Pb(II) and Th(IV) using Tulsion T-42 NH^+ form as cation organic exchange resin, in the presence of different concentration of ammonium sulfamate (0.01 - 2.0M). According to the given Results in Table (1), it was found that the distribution coefficient for Th(IV) is completely sorption at lower sulfamate concentration (0.01 - 0.7M), due to the formation of positively charged complexation. However, this metal ion exhibit also another trend, where their K_d values decrease i.e., the sorption process is reduced at higher concentrations of $NH_2 SO_2 NH_4$ solution, this previous behavior becomes more pronounced for other metal ions as the tendency of these elements, which is used to form charged complex ions, increases or decreases. Our results agree well with those of korkisch (15) and other (2) who used THF - water - 20% HCl and isopropanel- water - 1.0 MHCI mixture respectively.

Table (1) indicates, the K_d - values of Hg(II) are lower in all systems under study. This lowering in the sorption is probably due to the formation of neutral sulfamate complexes, which is predominantly either $Hg(Hg N SO_3)_2$ or the mercuric oxy-sulfamate (16). Two hydrogen atoms of the - NH_2 group are substituted readily with Hg(II) to form the compound Hg - NSO_3 - NH_4[16], but the formation of normal mercuric sulfamate, $Hg(NH_2SO_3)_2$ was very few (17, 18). At the same time, the formation of Hg - ammonia complex i.e. $[Hg(NH_3)_2](NO_3)_2$ and / or $Hg[NH_2 NO_3]$ also decrease/-s the sorption on the resin.

Moreover, in case of Mg(II), Ni(II), Zn(II), Cd(II) and Cu(II) ions, the sorption of these metal ions decreases with the increasing of ammonium sulfamate concentrations, whereas the K_d - values, of these metals will be 291, 288, 274, 259 and 257 at 0.01M sulfamate with respect to the following metal ions Cd(II) > Ni(II) > Mg(II) > Cu(II) > Zn(II) respectively. However, at lower concentration, the positively charged complexes are formed for these elements, i.e. M^{ll} $(NH_2SO_3)_2$; while at the higher concentration of sulfamate solution or neutral species i.e. M^{ll} $(NH_2SO_3)_2$ (19) is formed what results in a more decrease in the uptake. This change becomes more as the affinity of metal ions to form negatively charged ions increases. Pb(II) ions could not be detennined in the range of (0.7 - 2.0M sulfamate), because an insoluble compound is formed. This precipitation is probably due to the formation of lead sulphate ($PbSO_4$) (20).

The results in Table (1) indicate that the metal ions in the present study may be divided into different groups with varying concentration of dioxan solvent (10%, 20%, 30% and 40% (v/v), with increasing sulfamate concentrations. First the group of metal ions, which include Zn(II), Cd(II) and Cu(II), gives high absorbed by the exchange resin at the fixed eluting agent. While the second group includes Mg(II) and Ni(II) at fixed concentration of sulfamate solution (0.01 - 0.1M) is highly absorbed from the system at higher dioxan solution, while at (0.3 - 2.0M) at all proportion of dioxan a decrease in K_d - values may be reached to zero. The K_d - values could not be detennined for the third group in case of Pb(II) in the range of (0.05 - 2.0M) sulfamate solution. Moreover in case of Fe(III) ions at 20% (v/v) dioxan media gives a higher K_d - values and then gradual decrease with 30, 40% (v/v) dioxan solution. It has been seen from the behavior of these metal ions under study that the addition of organic solvent to water-sulfamate system leads to further modification of the selectivities in a number of cases (2), and thus leads to a possible separation which is otherwise unattainable in aqueous medium. Moreover, Th(IV) ions do not exhibit an increase in or decrease in dioxan medium at lower sulfamate concentration, i.e. completely sorption was observed.

In general, the addition of water-miscible organic solvent enhances the complexations, as the dielectric constant of the mixed solution decreases (20). In these studies, the aqueous phase contains dioxan in different proportions 10%,20%, 30% and 40% (v/v). This mixture favors the complexation and consequently. reduces the free metal ions concentrations at a higher sulfamate solution; the result is less sorption onto the resin.

The separation of elements; although the K_d - value is measured using the bath

technique, it may indicate the elution behavior of metal ions on an ion exchange column. The prepared resin column had a length of 50 cm and a diameter of 1.2 cm. To separate two metal ions, the elution conditions are chosen such that one of the metal has a very high K_d and thus retained by the column, and the other metal ion has a very low of distribution coefficient value, which is reached to unity or zero, so that the metal ion may be eluted with a small volume of eluting agent. From the distribution data, based on the effect of sulfamate concentration, aqueous, aqueous - dioxan - sulfamate media, it is possible to separate Hg(II) from the most metal ions under study, Fe(III) from Mg(II) at 2.0M - 10% (v/v) dioxan solution, Fe(III) from Ni(II) at 30% (v/v) dioxan 1.0M sulfamate system. While Th(IV) has a very high K_d- values at all system studies, therefore Th(IV) could be separated from the all metal ions under study.

Separation of Some Binary Systems of Metal Ions (3, 5, 15):

The Tulson T - 42 - NH_4 dry resin was put into the column described above, and it was firstly washed with 0.01 M $NH_2 SO_3 NH_4$ solution, 2 mg of $Fe(NO_3)_3$ solution was mixed with 2mg of $Hg\{NO_3)_2$ solution, then the mixture was passed through the column at a flow rate of 3.0 ml/1min. 30ml of 0.7 M ammonium sulfamate solution was passed through the column at the same previous rate. This volume is quite enough to elute Hg(II) out. Fe(III) was next eluted with 95 ml of 0.1 MHCl solution. The concentration of both Hg(II) and Th(IV) ions were determined quantitively with standard solution of EDTA - disodium salt. Amount recovered (Hg - 1.88 mg) and Fe(III) - 1.91 mg.

The same procedure was used for the separation of Th(IV) and Hg (11) ions. Table (1) shows that the K_d - values could be used to arrive at optimum conditions for the separation of these elements. Thus, at 0.7 M sulfamate solution, 40% (v/v) dioxan, it is possible to separate Hg (11) from Th(IV). The amount (recovered) that has been taken for the two ions, were 2.0 mg (1.96 mg) for Hg (11) and 2.0 mg (1.82 mg) for Th(IV), in 100 ml (0.5 ml) HCl solution. The separation of Hg(II) from Mg(II), Cu(II), Ni(II), Zn(II) and Cd(II) is also possible at 0.7 M sulfamate solution - 10, 20% (v/v) dioxan solution at different elution volumes.

Based on the results of the present study, Mg(II) from Ni(II), Fe(III), Zn(II), Cd(II) at 2.0 M sulfamate - 10% (v/v) dioxan solution using the procedure mentioned earlier. The first elution solvent, which is required to elute Mg(II), was 2.0M sulfamate - 35 ml. Fe(III) was the next eluted with 0.5M HNO_3 solute 65ml. The amount (recovered) that has been taken, were 2.0 mg (1.86mg) for Mg(II) and 2.0 mg (1.94 mg) for Fe(III).

Table (I): Variation of K_d - values of some metal ions (O.IM) with percentage of dioxan in presence of Tulsion T-42 NH_4 cation exchange resin in ammonium sulfamate solution.

Metal ions	Dioxan; % (v/v)	Ammonium sulfamate solution; M.							
		0.01	0.05	0.1	0.3	0.7	1.0	1.5	2.0
M(II)	0.00	274.39	229.41	142.86	89.47	66.32	20.20	8.14	3.45
Ni(ll)	0.00	288.11	234.56	190.47	136.36	75.27	52.63	32.34	28.16
Fe(III)	0.00	193.70	189.34	174.40	135.60	129.21	116.67	91.88	70.70
Zn(ll)	0.00	257.78	234.50	213.22	145.25	78.94	51.28	47.18	36.12
Cd(II)	0.00	291.16	253.30	208.34	153.41	79.00	62.83	43.45	25.12
Cu(II)	0.00	259.81	237.50	242.04	104.03	94.45	70.27	63.78	61.62
Pbal)	0.00	278.18	253.00	212.00	189.16	ppt	ppt	Ppt	ppt
He(ll)	0.00	36.41	32.22	25.76	8.01	0.0	0.0	0.0	0.0
Th(IV)	0.00	C.s	C.s	C.s	C.s	315.2	132.14	117.90	92.66
Meal)	10	297.70	235.90	180.92	71.36	33.51	15.60	2.15	0.00
Ni(1I)	10	286.99	245.17	202.15	121.18	55.49	41.50	25.77	22.91
Fe(III)	10	197.00	191.00	173.00	111.06	56.22	51.70	26.29	14.00
Zn(II)	10	259.17	234.65	194.11	140.46	63.17	46.63	42.50	29.34
Cd(II)	10	281.18	212.0	200.95	112.70	62.62	42.36	37.28	15.75
Cu(II)	10	260.90	240.61	213.1	100.16	90.76	61.83	45.21	40.28
Pbal)	10	195.0	ppt	ppt	ppt	ppt	ppt	Ppt	ppt
H(l1)	10	41.66	28.16	22.90	8.50	0.0	0.0	0.0	0.0
Th(IV)	10	C.s	C.s	C.s	316.70	280.10	130.00	117.00	90.77
M(II)	20	305.19	251.32	217.00	63.52	27.44	9.80	1.11	0.00
Ni(II)	20	291.64	271.19	221.16	112.10	39.18	33.20	21.14	18.18
Fe(III)	20	208.00	197.76	170.06	93.02	42.73	7.04	0.00	0.00
Zn(II)	20	260.00	234.56	194.02	140.45	63.15	41.45	37.77	25.0
Cd(ID	20	220.53	205.0	200.36	92.50	59.83	35.10	29.06	8.21
cual)	20	260.90	215.0	152.40	61.80	50.20	33.82	25.6	23.7
Pb(II)	20	170.91	ppt	ppt	ppt	ppt	ppt	ppt	ppt
HdII)	20	45.53	26.25	22.76	12.76	0.00	0.00	0.00	0.00
Th(lV)	20	C.s	C.s	C.s	192.15	140.0	121.0	115.12	75.79
Mg(11)	30	321.81	265.21	225.18	59.57	19.47	3.78	0.00	0.00

Ni(ID	30	295.53	285.97	238.37	104.39	17.01	14.90	4.35	2.29
Fe(III)	30	199.00	175.11	140.00	24.25	17.50	0.00	0.00	0.00
Zn(II)	30	260.00	234.56	191.20	140.15	62.00	35.02	32.00	21.00
Cd(ll)	30	205.07	203.70	198.17	83.10	40.01	28.90	17.60	2.00
Cu(II)	30	210.71	148.81	91.88	42.0	37.08	22.32	17.20	13.8
Pb(II)	30	151.00	ppt	Ppt	ppt	ppt	ppt	ppt	ppt
82(11)	30	42.19	23.0	20.20	0.00	0.00	0.00	0.00	0.00
Th(lV)	30	C.S	C.S	213.5	160.0	121.89	80.79	65.51	40.30
M2(11)	40	324.99	277.88	231.23	56.09	8.41	1.21	0.00	0.00
Ni(11)	40	310.46	295.18	280.11	71.20	9.8	5.12	0.00	0.00
Fe(III)	40	195.57	151.90	121.10	9.55	4.03	0.00	0.00	0.00
Zn(ll)	40	260.00	234.56	189.99	138.78	16.19	31.47	27.12	21.86
Cd(ll)	40	198.61	193.43	190.75	70.70	30.52	21.80	4.00	0.00
Cu(11)	40	141.10	121.99	71.68	35.54	24.47	18.88	12.38	6.20
Pb(11)	40	150.0	ppt	Ppt	ppt	ppt	ppt	Ppt	ppt
82(11)	40	39.25	21.35	17.92	11.0	0.00	0.00	0.00	0.00
Th(1V)	40	C.S	C.S	213.0	160.0	121.00	80.00	56.0	40.00

Note: c.s = completely sorption
ppt = precipitation

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