CATION- EXCHANGE BEHAVIOUR OF SEVERAL ELEMENTS IN NITRIC ACID- ORGANIC SOLVENT MEDIA

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Abstract

Distribution coefficient studies of the metal ions Ni^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Co^{2+} and Zn^{2+} on stannic silicomolybdate (H^+ form) were performed in aqueous and aqueous- organic solvent systems having different dielectric constants namely ethanol, ethylene glycol and glycerol. The effect of organic solvent percentage and temperature on the distribution coefficient was explored. The efficiency of this cation exchanger in different experimental conditions was established. Due to the large difference in the distribution coefficient values, separations of the metal ions from their mixture were performed. It was finally concluded that the 50 °C appeared to be the most favorable temperature. Important quantitative separations of metal ions in binary mixtures including Cu^{2+}- Pb^{2+}, Cu^{2+}- Co^{2+}, Cu^{2+}- Al^{3+}, Ni^{2+}- Pb^{2+}, Ni^{2+}- Al^{3+}, Zn^{2+}- Pb^{2+}, Zn^{2+}- Co^{2+}, Zn^{2+}- Al^{3+}, Cr^{3+}- Pb^{2+} and Ni^{2+} - Co^{2+}; were performed.

Introduction

Inorganic ion exchangers are in general superior to organic exchanger in some aspects such as their resistance to the high ionizing radiation and can be used at elevated temperatures without any danger of decomposition[1, 2]. Moreover, they often exhibit specificity towards certain metal ions. For these reasons, there has been a revolutionary growth in the field of synthetic ion exchangers[3].

In recent years, there has been a growing concern with environmental protection. The presence of heavy metals in the enviroment has been shown to be detrimental to a variety of living species including human beings. The removal of heavy metals received considerable attention because of their association with various health problems. Companies that use chromic acid for electroplating, anodizing and other surface finishing operations have a difficult and costly procedure used to treat wastewater disposals contaminated with chromic acid. [4].

In all metal- finishing operations, chromic acid is reduced to Cr^{3+} and metal salts are formed by dissolution of the metals. Toxicological studies have shown that the degree of toxicity of some elements such as Pb^{2+}, Ni^{2+}, Al^{3+}, Co^{2+}, Ba^{2+} ... etc., depends on the chemical form in which the element is present.

Different technologies, i.e., reverse osmosis, electrolytic recovery techniques and liquid- liquid extraction, among others, have also been employed worldwide[5]. More recently, new membrane technologies have been investigated by different research groups since membranes offer a flexible, modular energy-efficient device with a high specific surface[6, 7].

Lead has been found to be[8] acute toxic to human beings when present in high amounts (e.g. > 15 µg/L, in drinking water). Lead is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, and weakness of muscle, hallucination and renal damages.

A mort comprehensive survey has been undertaken by many authors[9-12] who determined K_d- values for elements in mineral acid, containing methanol, ethanol, n- propanol, isopropanol, ethylene glycol, acetic acid, tetrahydrofuran and acetone as organic solvents. Attention has been focused mainly on elements having tendencies to form halo complexes, which showed spectacular increase in their affinities to resin.

This paper presents results on the ability of stannic silicomolybdate to removal and separation of the metal ions studied herein in aqueous and aqueous-organic solvent solutions. Batch experiments examine the effect of dielectric constants and temperature.

Experimental
Reagents and chemicals:
Stannic (IV) chloride pentahydrate (Loba Chemie, India). Sodium molybdate (M & B, USA). Sodium metasilicate (CDH. India). Nitrate of metal ions and ethanol, ethylene glycol and glycerol (E. Merch India) used were of analytical grade.

Syntheses:
Stannic silicomolybdate was prepared[13] by adding a mixture of 0.1 M aqueous solutions of sodium molybdate and sodium metasilicate to a 0.1 M aqueous solution of stannic chloride pentahydrate with constant stirring in a 1:1 volume ratio. The pH (0.63) of the resulting solution was maintained by adding 1 M HNO_3. The resultant mixture containing the precipitate was divided into two equal portions; one of the portions was filtered directly and the other one was refluxed for 6 h. The subsequent steps are the same as described before. The supernatant liquid was tested to ensure for the complete utilization of the reagents. The liquid is separated from the precipitates by decantation. The precipitate was washed with DMW several times; filtered and washed again to remove reagents adhered to the precipitates. The final product was dried at 40 ± 2 °C in a electrically controlled oven. The material was cracked into fine particles when immersed in water. It was converted into the H^+ form by treating with   1.0 M HNO_3 solutions. It was finally rinsed with DMW to remove excess acid in a column and dried in an oven at 40 ± 2 °C.

Distribution studies:
The distribution coefficient (K_d) for metal ions Ni^{+2}, Ba^{+2}, Al^{+3}, Cr^{+3}, Cu^{+2}, Pb^{+2}, Co^{+2} and Zn^{+2} was determined in aqueous and a number of mixed systems viz.

aqueous ethanol, aqueous- ethylene glycol and water- glycerol. The effect of temperature on the distribution coefficient was also studied. Stannic silicomolybdate (1.0 g) in the H^+- form was put into 100 ml conical flask each containing 50 ml of the desired mixed system solution of 5×10^{-4} M concentration of metal ions. The mixture was continuously shaken for 5 h at 25, 50 and 70 °C. The amount of metal ions present in the solution was determined by titrating it against disodium salt of EDTA using standard procedures[14]. K_d- values were calculated by using the following relationship[13]

$$K_d = \frac{(1-F)/1.0 \text{ g}}{(1-F)/50 \text{ ml}} = \frac{(1-F)}{F} \times 100$$

Where 1 is the volume of EDTA used before treatment with the exchanger, F is the volume of EDTA used after treatment, and 1-F is the amount of metal ion in the resin phase.

Separations

In order to explore the separation ability of stannic silicomolybdate by column chromatography, a number of binary quantitative separations of metal ions were practically accomplished. Stannic silicomolybdate (5.0 g) in H^+ form (50- 100 mesh) was packed in a column with a glass wool support at the base. A mixture of metal ions solution to be separated was then poured into the column. The solution was allowed to move through the column at the rate of 8- 10 drops / min. and recycled at least three times. The column then washed with DMW to rinse the sides of the column. The adsorbed metal ions were then eluted with appropriate eluents. The flow rate of the effluent was maintained at 1 ml / min. throughout the elution process. The effluents were collected in 10 ml fractions and metal ions contents have been determined titrimetrically against EDTA solution.

Discussion

The distribution coefficient values presented in Table 1 show that the affinity of almost all metal ions modifies the selectivities in a number of cases (K_d-values of some elements) and thus indicating separation possibilities which are wise other unattainable in aqueous medium. Different reports on such subject have been reported[15, 16] demonstrated the usage of mixed organic solvents namely ethanol, ethylene glycol and glycerol. According to the important role played by these organic solvents on the K_d- values of the cation studied in the present work, the behaviour of the cation can be divided into three groups with varying concentration of organic solvents (15, 40 and 60% v/v) at constant acidity 0.01M HNO_3. The first group of the metal ions has a considerable high K_d- value by the cation exchanger and gradual increase with increase ethanol, ethylene glycol or glycerol concentration. A number of metal ions such as Ni^{+2}, Ba^{+2}, Al^{+3}, Cr^{+3}, Cu^{+2}, Pb^{+2}, Co^{+2} and Zn^{+2} show increase in their K_d values with gradual increase ethanol concentration. This increase of K_d- values is due to the complexation of metal ions with ethanol resulting in the formation of positivity charged metal- ligand species[17]. As the concentration of ethanol is further increased the number of neutral or low positively charged species increases by their causing decrease in the K_d- values of Pb^{2+} and Al^{3+} ions up to 60% v/v.

The effect of increasing ethylene glycol on K_d- values for many elements are shown in Table 1, where the K_d- values are increased for many ions, such as

Ba^{2+}, Co^{2+} and Al^{3+}, then sudden decrease occurred for the K_d- values up to 60% v/v, while the other ions, namely: Cu^{2+}, Ni^{2+}, Cr^{3+} and Zn^{2+} show Sharp decrease in the K_d- values with addition of ethylene glycol. Exception occurs for Pb^{2+} ion, where a decrease in its Kd- value up to 15% v/v ethylene glycol took place then sudden increase occurred at 60% v/v. The very low K_d- values of Cu^{2+}, Ni^{2+} and Zn^{2+} from 15 to 60% v/v ethylene glycol suggest the formation of either a large number of neutral species having very low dissociation or negatively charged species[9, 18].

Moreover, similar behaviour in glycerol for Ba^{2+}, Ni^{2+}, Cr^{3+}, Pb^{2+}, Zn^{2+}, Co^{2+} and Al^{3+} ions was observed. These ions tend to form positively charged complexes with increasing glycerol concentration up to 40% v/v and then a drop in their K_d- values occurs when the percentage of glycerol increased.

Influence of temperature

To determine the effect of temperature on the exchange process, 1.0 g of stannic silicomolybdate was equilibrated with 50 ml of desired aqueous- solvent system for 4 h at different temperatures including 20, 35 and 50 °C. The concentration of the reagent after equilibration was determined by titration with disodium salt of EDTA using standard procedures[14].

An increase in K_d- values for all metal ions studied, namely Ni^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Co^{2+} and Zn^{2+} with a raise in temperature as shown in Table 2. Concerning the effect of the temperature on the exchange process, the metals uptake is favored by raising the temperature, since a higher temperature activates the metal ions for enhancing the exchange process. Also, it the cations move faster with increasing temperature. Likely explanation for this is that retarding specific or electrostatic, interactions become weaker and the ions become smaller, because solvation is reduced [19].

Prediction of separation possibilities: In the present work, batch distribution coefficients were used as a guide for the selection of separation conditions. The volume required to elute a metal ion from a column agreed favourably with the volume predicted by the distribution coefficient data. To separate two metal ions from each other on a cation exchange column, the solvent composition and nitric acid concentrations were chosen such that one metal will be rapidly eluted from the column (K_d should be low, preferably one or less) while the other metal ions has a high K_d value and is tightly held by the column. The stannic silicomolybdate column had a length of 30 cm and diameter 1.2 cm. Taking care that no air bubbles were introduced into the beds.

Zero and very low K_d- values (~3) of Cu and Ni^{2+}, at 0.01 M HNO_3- 60% v/v glycerol, Cu^{2+}, Ni^{2+} and Zn^{2+} at 0.1 M HNO_3- 40- 60% ethylene glycol and Cr^{3+} at 0.1 M HNO_3- 60% ethylene glycol indicates its separation from all other metal ions (Table 3).

Thus, a number of binary separations, namely, Cu^{2+}- Pb^{2+}, Cu^{2+}- Co^{2+}, Cu^{2+}- Al^{3+}, Ni^{2+}- Pb^{2+}, Ni^{2+}- Al^{3+}, Zn^{2+}- Pb^{2+}, Zn^{2+}- Co^{2+}, Zn^{2+}- Al^{3+}, Cr^{3+}- Pb^{2+} and Ni^{2+}- Co^{2+} were achieved quantitatively from a synthetic mixture on a column of stannic silicomolybdate Table 2 at 25 °C.

Conclusions:

Stannic silicomolybdate as an inorganic cation exchanger has been used to remove target pollutants Ni^{2+}, Ba^{2+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Pb^{2+}, Co^{2+} and Zn^{2+} ions from aqueous- solvent media.

Batch and column methods were done for the separation of Pb^{2+}, Co^{2+} and Al^{3+} from the binary mixture with other metal ions from synthetic and a few real life samples. The efficiency of this cation exchanger in different experimental conditions was established and because of the large difference in the distribution coefficient values separation of the metal ions from their mixtures was possible.

Table 1: Effect of concentrations of organic solvents on the K_d- values at 20 °C

Metal ions Solvents	%	Ba^{2+}	Cu^{2+}	Ni^{2+}	Cr^{3+}	Pb^{2+}	Zn^{2+}	Co^{2+}	Al^{3+}
Ethanol	0.0	90	35	70	110	480	98	200	130
	15	125	50	110	150	520	170	240	160
	40	140	100	160	180	600	220	300	200
	60	60	130	200	290	370	260	380	105
Ethylene glycol	0.0	210	35	70	110	400	98	200	130
	15	90	27	30	192	250	20	360	170
	40	60	3.0	0.0	70	250	0.0	420	300
	60	20	0.0	0.0	2.0	330	0.0	180	209
Glycerol	0.0	50	35	70	110	400	98	200	130
	15	90	80	115	181	570	100	250	190
	40	140	140	166	250	630	98	300	222
	60	90	0.0	0.0	90	370	98	215	221

Table 2: Effect of temperature on the K_d- values

Metal ions Solvents	%	Temp. °C	Ba^{2+}	Cu^{2+}	Ni^{2+}	Cr^{3+}	Pb^{2+}	Zn^{2+}	Co^{2+}	Al^{3+}
Glycerol	0.0	25	90	35	70	110	400	98	200	130
		35	98	60	115	130	470	180	210	142
		50	100	80	170	190	550	200	210	170
	15	25	140	80	115	181	570	190	250	190
		35	150	98	118	200	600	200	270	194
		50	164	207	118	203	620	210	318	201
	40	25	192	140	166	250	630	240	300	222
		35	200	152	180	266	647	270	330	240
		50	260	180	210	280	700	291	332	269
	60	25	50	0.0	0.0	90	370	160	215	221
		35	67	1.2	2.0	110	399	171	230	243
		50	90	1.5	2.0	148	500	200	250	300

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Table 3: Possible binary separations of metal ions in aqueous- organic solvent systems.

Eluting agents mixture contents	Taken mg	Found mg	Recovery %
Cu^{2+} - Pb^{2+}			
Cu^{2+}- 40% (v/v) ethylene glycol- 0.01 M HNO_3 / Pb^{2+} 2.0 M HNO_3.	10 10	9.7 9.9	97 99
Cu^{2+}- Co^{2+}			
Cu^{2+}- 40% (v/v) ethylene glycol- 0.01 M HNO_3 / Co^{2+} 2.0 M HNO_3.	10 10	9.7 9.8	97 98
Cu^{2+} - Al^{3+}			
Cu^{2+}- 60% (v/v) glycerol- 0.01 M HNO_3 / Al^{3+} 2.0 M HNO_3.	10 10	9.9 9.8	99 98
Ni^{2+}- Pb^{2+}			
Ni^{2+}- 40% (v/v) ethylene glycol- 0.01 M HNO_3 / Pb^{2+} 2.0 M HNO_3	10 10	9.9 9.7	99 97
Ni^{2+}- Al^{3+}			
Ni^{2+}- 60% (v/v) glycerol- 0.01 M HNO_3 / Al^{3+} 2.0 M HNO_3	10 10	9.9 9.9	99 99
Zn^{2+}- Pb^{2+}			
Zn^{2+} - 60%(v/v) ethylene			

glycol- 0.01 M HNO_3 / Pb^{2+} 2.0 M HNO_3	10	9.9	99
Zn^{2+}- Co^{2+}	10	9.8	98
Zn^{2+}- 40% (v/v) ethylene glycol- 0.01 M HNO_3 / Co^{2+} 2.0 M HNO_3	10	9.8	98
Zn^{2+}- Al^{3+}	10	9.7	97
Zn^{2+}- 40% (v/v) ethylene glycol- 0.01 M HNO_3 / Al^{3+} 2.0 M HNO_3	10	9.9	99
Cr^{3+}- Pb^{2+}	10	9.7	97
Cr^{3+}- 60% (v/v) ethylene glycol- 0.01 M HNO_3 / Pb^{2+} 2.0 M HNO_3	10	9.6	96
Ni^{2+}- Co^{2+}	10	9.8	98
Ni^{2+}- 60% (v/v) glycerol- 0.01 M HNO_3 / Co^{2+} 1.5 M HNO_3	10	9.7	97
	10	9.8	98

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سلوكيات التبادل الكاتيوني لعدد
من العناصر في أوساط حمض النتريك مذيبات عضوية

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الملخص:

تمت دراسة معامل التوزيع لأيونات الفلزات نيكل ، باريوم ، ألومنيوم ، كروم، نحاس ، رصاص ، كوبلت و زنك على المبادل الكاتيوني ستانيك سليكومولبيدات في الشكل الهيدروجيني في أنظمة مائية ومائية عضوية ذات ثوابت عزل مختلفة وهي: الإيثانول ، الإيثلين جليكول و الجليسرول. كما تمت دراسة وتوضيح تأثير النسبة المئوية للمذيب العضوي وكذلك درجة الحرارة على معامل التوزيع. ومن هذه التجارب تمت معرفة كفاءة هذا المبادل الكاتيوني وبسبب الفروق الكبيرة لقيم معامل التوزيع أمكن إجراء عمليات فصل لبعض ايونات الفلزات سابقة الذكر من مخاليطها. وقد تم استنتاج ان درجة الحرارة المثلى للحصول على أعلى قيم لمعامل التوزيع كانت 50 درجة مئوية. كما تم إجراء عمليات فصل كمي لبعض ايونات الفلزات من مخاليطها الثنائية مثل نحاس– رصاص ، نحاس– كوبلت، نحاس– الومنيوم ، نيكل– رصاص ، نيكل– الومنيوم ، زنك– رصاص ، زنك– كوبلت ، زنك– الومنيوم ، كروم– رصاص و نيكل– كوبلت.