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SORPTION OF 60 ELEMENTS ON CATION EXCHANGE RESINS IN AMMONIUM ACETATE SOLUTIONS.

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Abstract: The distribution coefficients of alkali metals, alkaline earths metals, transition metals, poor metals, non-metals, lanthanide series, and actinide series elements on cation-exchange resins (Dowex 50w-x8) was determined in ammonium acetate solution. The concentrations of the ammonium acetate solutions used ranged from 0.1 to 5 M. The determined sorption for all elements is discussed and analyzed. This data is significant for more efficient separations and purifications of these elements.

Key words: distribution coefficients, ion-exchange resins, ICP-MS, ammonium acetate.

1. Introduction

There are a lot of experimental data for the sorption and the separation of elements by ion exchange resin.[1]–[11]. Within recent years, the availability of stable high capacity ion exchange resins has led to the rapidly increasing use of these materials in the analytical field.[12]–[14] Different radionuclides are used for diagnosis and therapy in nuclear medicine. Ion-exchange resins are often used in their preparation, separation and conditioning for the synthesis of radiopharmaceuticals. It is appropriate to use an ammonium acetate medium for medical application. Ammonium acetate is often used as a buffer for coupling a radionuclide with a chelator that promotes sequential binding to the antibody. Acetate media has no chemically and biologically adverse for body by their range of Ph.[15]–[20] The published distribution coefficient data for cation-exchange resin in ammonium acetate medium is very limited. Data is available only for alkaline earth element.[21]

2. Experimental

In this study, distribution coefficients were determined for 60 elements, across a range of ammonium acetate molarities with cation-exchange resin (Dowex 50x8). The elements used for this research are Li, Rb, Cs, Be, Sr, Ba, Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Th and U.

Materials and methods

2.1. Reagents and materials

The amount of elements was determined by ICP-MS. The measurements were made using the standard parameters: a radio frequency (RF) generator with power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 12 L/min; an auxiliary Ar flow rate of 0.9 L/min; an Ar flow rate into the nebulizer of 0.9 L/min and an analyzed sample flow rate of 0.8 mL/min.

The cation-exchange resin (Dowex 50w-x8 in H⁺ form) is a strong acid cation-exchange resin containing 8% DVB with water retention capacity between 50 and 58%, total exchange capacity – 1.7 meq/mL, mesh size 200 – 400. [12]

The cation-exchange resin (Dowex 50w-x8) in H⁺ form was modified into NH₄⁺ form: The resin was washed with 30ml of HCl (4M) acid then CH₃COONH₄ (4M) solution and 30ml of distilled water. The resin was air-dried 72 hours at room temperature.

Three set of multi-elements standard solutions were used.

Standard (A) is a 10mg/l multi-element ICP-MS calibration standard in 0.3M nitric acid containing the elements Al, As, Ba, Be, B, Cd, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, La, Pb, Li, Lu, Mn, Nd, Ni, Re, Rb, Sm, Sc, Se, Sr, Tl, Th, U, V, Yb, Y, Zn.

Standard (B) is a 10mg/l multi-element ICP-MS calibration standard in 0.3M HNO₃ + Traces of HF containing the elements Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, Zr.

Standard (C) is a 10mg/l multi-element ICP-MS calibration standard in 0.6M HCl acid containing the elements Au, Ir, Os, Pd, Pt, Rh, Ru.

2.2. Distribution coefficients (K_d)

Distribution coefficients are a very useful parameter in ion exchange chromatography for effective separation of elements, dissolved in a solution. K_d gives us information about sorption of elements on the resin in different solutions.

Distribution coefficient were calculated by equations 1.

$$K_d = \frac{C_B - C_A / W}{C_A / V} \quad (1)$$

C_B - the elemental concentrations in micrograms per mL of solution before equilibration

C_A - the elemental concentrations in micrograms per mL of solution after equilibration

W - is the weight of dry DOWEX resin in grams.

V - is the volume of CH₃COONH₄ solution in milliliters. [2], [8]

The method for the K_d-value determination

For the determination of the distribution coefficients, 2 ml of each standard (A, B+ C) were evaporated to wet salt. Each of the salt samples were diluted with 2ml of 0.1M ammonium solution that was used as stock solutions (I and II). The Stock Solution I and II consisted of the elements from standard A and standard B+C respectively. 2 ml of the initial solutions with different concentrations of CH₃COONH₄ (0.1, 0.3, 1, 2, 3,4 and 5M) were prepared. 0.25 ml of the stock solution (I and II) were added to the initial solutions. Then 1ml of the initial solutions was added to each Sample containing 50 mg resin. Finally, each sample contained 100µg/l of the

multi-element Standard (A or B+C) in the specific concentration of ammonium acetate and ion exchange resin. The Samples were left to reach equilibrium for 24 hours and were periodically shaken.

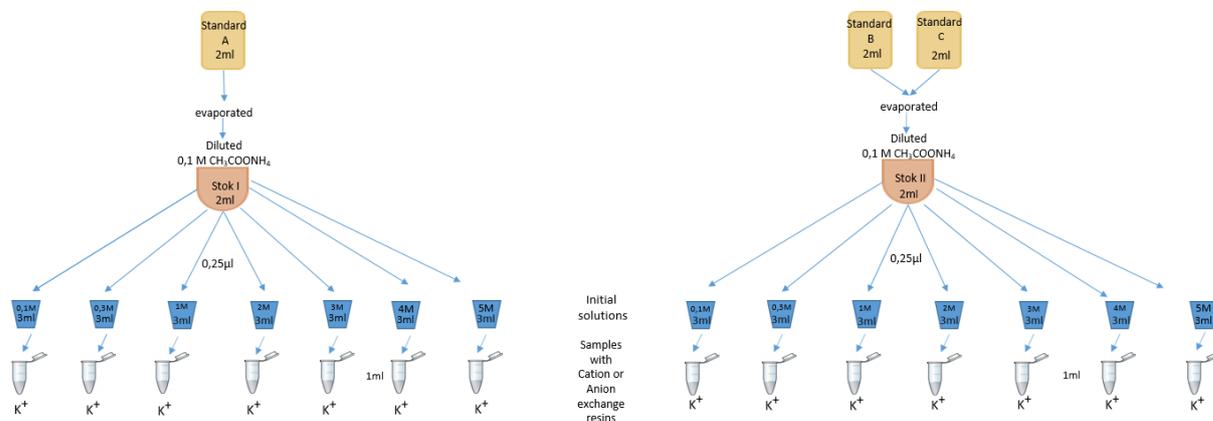


Fig. 1. Scheme of chemical procedure for K_d determination.

After that, 0.5 ml aliquot solution was taken from each sample, was diluted by 0.1 ml HNO_3 and deionized water to 5 ml. The rest 1ml of the Initial Solutions were diluted by 0.1ml HNO_3 and deionized water to 5ml. Then the samples and Initial Solutions were measured by inductively coupled plasma mass spectrometry (ICP-MS). (Fig 1)

3. Results

Figure 2 shows the distribution coefficients for 60 elements on cation-exchange resin with different concentrations of CH_3COONH_4 solution.

The alkaline and alkaline earth metals

The alkaline metals Li, Rb, Cs are monovalent elements and with high concentrations of CH_3COONH_4 solution, K_d values decrease. A decrease of the K_d values was observed for divalent alkaline earth metals (Be, Sr, Ba) with the increase of CH_3COONH_4 solution concentration.

Lanthanide series elements.

The lanthanide series La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu are trivalent elements. They strongly adsorb in low concentration. K_d values decrease with high concentrations of CH_3COONH_4 solution. There are not any retention from 2 to 5 molarity on this resin.

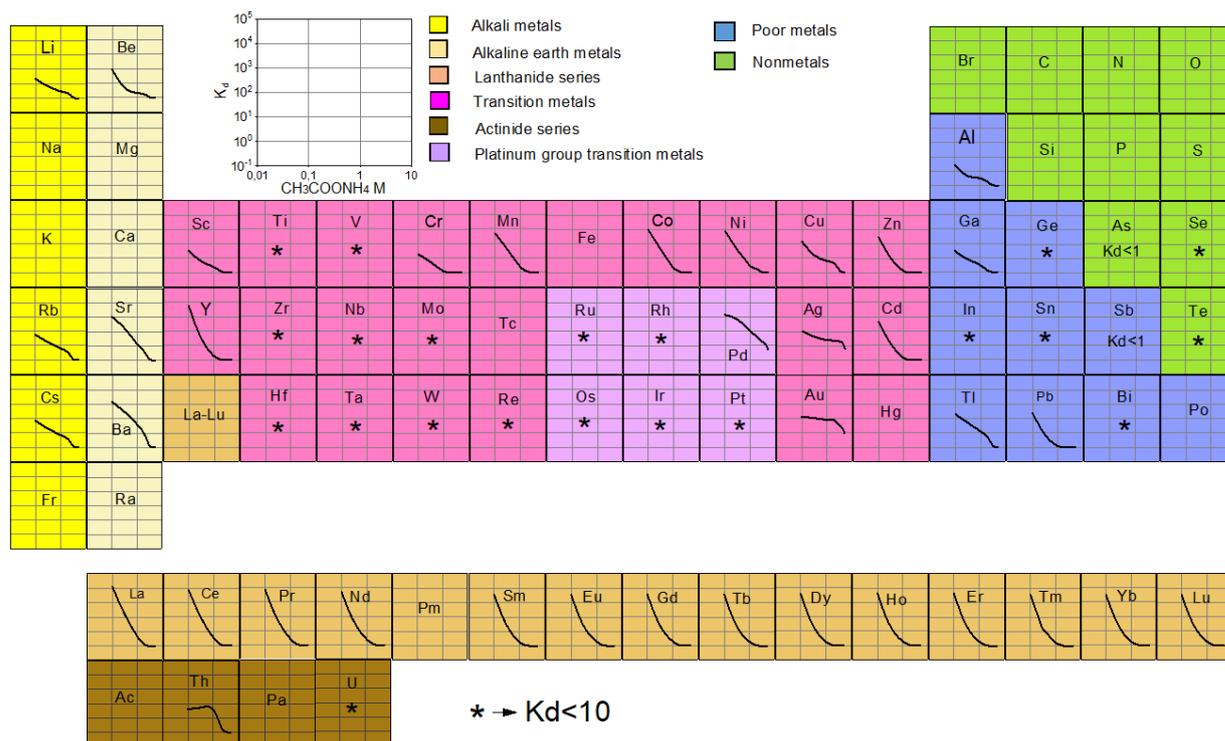


Fig 2. Distribution coefficients (K_d) of 60 elements on Dowex 50x8 in logarithmic scale as a function of CH_3COONH_4 concentration (measured at 0.1, 0.3, 1, 2, 3, 4 and 5 molarity).

Transition metals

The lanthanide series La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu as well as Sc and Y are trivalent elements that together form rare earth elements (REE). The K_d values for Sc and Y decrease with the increase of CH_3COONH_4 concentrations. Y show high retention at low concentration like lanthanides, but Sc show similar adsorption behavior like alkali metals. Au and Ag shows similar adsorption behavior on resin. These elements show retention at whole concentration range. The adsorption of Mn, Co, Ni, Cu, Zn and Cd is high at low concentration. Cr show some retention at 0.1 and 0.3 concentration. Ti, Zr, Hf, V, Nb, Ta, Mo, W and Re weakly adsorbed on the resin. Values of K_d for these elements are below ten.

Platinum group transition metals consist of the elements: Ru, Rh, Os, Ir, Pd and Pt. Pd show high adsorption at low concentration, with the high concentration decrease of the K_d values was observed. Ru, Rh, Os, Ir, Pt show weak retention on the resin with $K_d < 10$.

Poor metals, nonmetals and actinide group elements

Al, Ga, Tl, Pb are poor metals and with high concentrations of CH_3COONH_4 solution, K_d values decrease. Tl as monovalent element show adsorption behavior similar like alkaline metals. Sb is not adsorbed on the resin. In, Sn, Bi and Ge show weak retention on the resin with $K_d < 10$. Adsorption of As was found to be negligible over the whole ammonium acetate molarity range.

Se and Te are somewhat retained in the whole concentrations range with $K_d < 10$. Actinide series elements Th(IV) with the high concentration of CH_3COONH_4 solution the adsorption is increase and decrease again at high concentrations. U(VI) show weak retention on the resin with $K_d < 10$.

4. Discussion

Distribution coefficients on cation-exchange resin were determined with ammonium acetate solution for the 60 elements.

The cations of monovalent alkali and divalent alkali earth metals are easily sorbed by strongly acidic cation exchanger in ammonium acetate solution. It gives us advantage for the separation of these metals from elements, which show low retention.

The selectivity of the group-SO₃H increases with the increase in the atomic ionomer, the valence and degree of ionization of the exchanged ions, and decreases with the increase in the ionic radius of the hydrated ions. Selectivity decreases like for elements



in Dowex 50-8 in ammonium acetate solution. These series of selectivity are valid for dilute solutions. Low retention of Be at 0.3 molarity of solution allow to separate better element from Sr and Ba on cation exchange.

Sc, Y and lanthanides form only positive charged complexes and sorb as cations on Dowex 50X8. Lanthanide acetate system most probably does not contain anionic complexes at acetate concentrations.[22], [23] [24] Sc can be separated from other REE elements at 0.1 concentration of solution by eluting of Sc. High retention at low concentration allow to separate Y and lanthanides from Li, Ti, V, Cr, Ge, As, Se, Zr, Nb, Mo, Ru, In, Sn, Sb, Te, Cs, Hf, Ta, W, Re, Os, Ir, Pt, Bi, U.

The high retention of Mn, Co, Ni, Cu, Zn and Cd at low concentrations of solution on cation exchange can be explained the form of stable cation complexes in solution. The species present in solution for Mg, Co, Mn, Zn and Cd are also $\text{Me}(\text{H}_2\text{O})_6^{2+}$, $\text{Me}(\text{H}_2\text{O})_{6-z}(\text{CH}_3\text{COO})_z^{2+z}$, and $\text{Me}(\text{H}_2\text{O})_{6-2z}(\text{CH}_3\text{COO})_z^{2+z}$ form. The acetate ions are bonded as a monodentate ligand to the Mg, Co, Mn, and Zn cations and as a bidentate to the Cd cation. The cations also possess a second coordination shell of water molecules. Some indications have been obtained supporting the presence of hydration water around the acetate anions.[25]

In contrast, of other elements Ag and Au show good sorption at high concentration too. It gives us advantage to separate them from other elements at high concentration on cation exchange.

Zr and Hf ions undergo extensive hydrolysis and form aqua complexes. These complexes significantly decrease the sorption on the cation exchange resin.[26], [27] Cation exchanger poorly sorb Ti, Nb and Ta. In this way, these elements can be separated from other cations.

V, Mo, W and Re in neutral solutions are in an anionic form. At $\text{pH} > 5$ media V form anion complexes like $[(\text{VO})_2(\text{OH})_5^-]$ and $[(\text{VO})_2(\text{OH})_6^{2-}]$, Re anions specie like $[\text{ReO}_4^-]$. They are slightly sorbed by cation exchangers. [24], [26], [28] Platinum group metals easily form very strong complexes on anion exchanger and they are therefore poorly sorbed on the cation exchanger in ammonium acetate solutions. [24] In contrast of other platinum metals Pd show high adsorption on cation exchange. High retention at low concentration allow to separate Pd from other platinum group metals.

In acetate media Ga exist as hexaaqua ions like $\text{Ga}(\text{OH}_2)_6^{3+}$, Al form acetate ions like $[\text{Al}(\text{OOCCH}_3)]^{2+}$ and $[\text{Al}(\text{OOCCH}_3)_2]^+$. These ions easily sorbs by cation exchanger.[27]

There is the perspective for the separation of the poor metals, as Al, Ga and Tl have higher sorption than In in the range of 0.1 M – 0.3 M $\text{CH}_3\text{COONH}_4$ and high separation factors ($\beta > 3$).

As and Sb forms non-dissociating compounds with strong covalent bonds and has stronger bonds than Bi, Se and Te. These elements can be effectively eluted with ammonium

acetate solution from many elements. The ionic radii of Pb^{2+} is similar to that of Sr^{2+} ($\text{Pb}^{2+} = 1.19 \text{ \AA}$, $\text{Sr}^{2+} = 1.18 \text{ \AA}$) which can also help explain the steep inclination of the K_d trend.

Th(IV) forms stronger complexes with acetate like ThAc^{3+} , $\text{Th}(\text{Ac})_2^{2+}$, $\text{Th}(\text{Ac})_3^+$ in contrast of four valent elements (Ti, Zr, Hf) [29]. Th can be separated from Ti, Zr, Hf, U and many other elements. Cation exchangers are rarely used for the separation of uranium. Because the selectivity of resins for the cation UO_2^{2+} form are very low.

5. Conclusions

A broad survey of the cation exchange behaviors of 60 elements in $\text{CH}_3\text{OOCNH}_4$ solution is presented. The results are also summarized in the form of "Periodic Tables" which give the distribution coefficients of the elements as a function of $\text{CH}_3\text{OOCNH}_4$.

The results can be used for the future purification of 1, 2 and 3 valent elements on cation exchange resin by their high adsorption capacity for obtain substances which is used to get radiopharmaceuticals with the highest specific activity. The data can be applied for sorption and separation purposes for metals with different valences as well as ones of the same valence. Examples of possible individual separation of elements are given.

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KATION DƏYİŞMƏ SORBENTİ VASİTƏSİ İLƏ 60 ELEMENTİN AMMONİUM ASETAT MƏHLULUNDA SORBSİYASI.

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Xülasə: Ammonium asetat məhlulunda qələvi metalların, qələvi torpaq metallarının, keçid metallarının, zəif metalların, qeyri metalların, lantanoidlərin və aktinoid sırası elementlərinin kation dəyişmə sorbenti

(Dowex 50w-x8) vasitəsi ilə paylanma əmsalları müəyyən olunmuşdur. Ammonium asetat məhlulunun qatılığı 0,1 - 5 M arasında götürülmüşdür. Bütün elementlər üçün əldə olunan nəticələr analiz və təhlil olunmuşdur. Əldə olunan nəticələr göstərilən elementlərin effektiv təmizlənməsi və ayrılması üçün çox vacibdir.

Açar sözlər: paylama əmsalı, ion mübadilə sorbentləri, ICP-MS, ammonium asetat.

СОРБЦИЯ 60 ЭЛЕМЕНТОВ НА КАТИОНООБМЕННЫХ СМОЛАХ В РАСТВОРАХ АЦЕТАТА АММОНИЯ.

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Резюме: В растворе ацетата аммония были определены коэффициенты распределения щелочных металлов, щелочноземельных металлов, переходных металлов, бедных металлов, неметаллов, рядов лантанидов и элементов ряда актинидов на катионообменных смолах (Dowex 50w-x8). Концентрации используемых растворов ацетата аммония составляли от 0,1 до 5 М. Обсуждается и анализируется определенная сорбция для всех элементов. Эти данные важны для более эффективного разделения и очистки этих элементов.

Ключевые слова: коэффициенты распределения, ионообменные смолы, ICP-MS, ацетат аммония.