

Synthesis and Characterization of a Novel Metal Phosphonate—Zirconium (IV) Hydroxy Ethylidene Diphosphonate—and its Application in Separation of Metal Ions

Amit S. Jayswal and Uma V. Chudasama*

Applied Chemistry Department, Faculty of Technology & Engineering,
The M.S. University of Baroda, Vadodara-390001, India

✉ uvcres@gmail.com

Received May 18, 2007; revised and accepted August 2, 2008

Abstract: A novel hybrid ion exchange material, zirconium hydroxy ethylidene diphosphonate [ZrHEDP] of the class of tetravalent metal acid (tma) salt has been synthesized by sol-gel method. The material has been characterized for elemental analysis (ICP-AES), thermal analysis (TGA, DSC), FT-IR and X-ray diffraction studies. Chemical resistivity of the material in various media (acids, bases and organic solvents) have been assessed. ZrHEDP has been further probed for its utility as an ion exchanger. The Na^+ ion exchange capacity (i.e.c.) has been determined and effect of heating on i.e.c. studied. The distribution behaviour of ZrHEDP towards several metal ions has been studied in different electrolyte media/concentrations. Based on the distribution studies a few binary metal ion separations have been achieved.

Key words: Zr (IV) phosphonate, hybrid ion exchanger, zirconium hydroxy ethylidene diphosphonate, distribution coefficient, metal separations.

Introduction

There is currently high interest in engineering mixed materials of some organic-based inorganic ion exchangers, where features of the organic and inorganic components complement each other leading to the formation of new solid-state structures and materials with new composite properties (Clearfield, 1998) to give a wider range of applications. Such materials may also be termed as hybrid ion exchangers.

Tetravalent metal acid (tma) salts are the most widely studied group of inorganic ion exchangers, due to their excellent thermal stability and chemical resistivity. In this respect, tma salts have proved to be superior to many organic resins (Varshney, 1991 and Takahashi, 2002).

Tma salts have the general formula, $\text{M(IV)} (\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}$, where $\text{M(IV)} = \text{Zr, Ti, Ce, Th, Sn etc.}$ and $\text{X} = \text{P, Mo, W, As, Sb etc.}$ The protons present in the structural hydroxyl groups of these materials can be exchanged for several cations and thus they act as cation exchangers.

Zr (IV) phosphate, an inorganic ion exchanger of the class of tma salt, has been widely used as a cation exchanger and has shown a number of advantages as an ideal host lattice. In the tetrahedral moiety of phosphoric acid, $\text{PO}(\text{OH})_3$, if H or OH is replaced by R (where $\text{R} = \text{alkyl or aryl possessing ionogenic groups}$), phosphonic acids are obtained, which when treated with tetravalent metals such as Zr, Ti, Sn, Th, Ce, etc. give rise to metal phosphonates (Alberti, 1978; Mar Gomez-Alcantara, 2004). M(IV) phosphonates are of special interest, as they are very insoluble compounds and possess all the characteristics of an ion exchanger. Though several metal

*Corresponding Author

phosphonates have been synthesized and characterized, the focus has been on structure elucidation (Alberti, 1996; Clearfield, 1996).

In the present endeavour, a novel metal phosphonate (ZrHEDP) (where HEDP = hydroxy ethylidene diphosphonic acid), a hybrid ion exchange material of the class of tma salt, has been synthesized by sol-gel method and characterised. Though the potential use of metal phosphonate as an ion exchanger has been suggested, a literature survey reveals that no systematic studies have been carried out on the ion exchange characteristics of these materials.

The distribution coefficient, K_d towards Pb (II), Bi (III), Th (IV), Zn (II), Mn (II), Cu (II) and Ni (II) ions in different electrolyte media/concentrations has been determined and the utility of ZrHEDP as a cation exchange material has been demonstrated by carrying out some binary metal ion separations. The removal and recovery of toxic/heavy metals being an area of current interest, as a case study, the removal of nickel from an effluent has been demonstrated.

Experiment

Synthesis of ZrHEDP

ZrHEDP has been prepared by mixing aqueous solutions of [0.1 M, 250 mL] $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and [0.2 M, 250 mL] sodium salt of HEDP, dropwise and with constant stirring at $\sim 70^\circ\text{C}$. The gelatinous precipitates obtained was digested for one hour at $\sim 70^\circ\text{C}$, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature. The material was then broken down to the desired particle size [30-60 mesh (ASTM)] by grinding and sieving and further converted to the acid form by taking 5 g of the material and treating with 50 ml of 1 M HNO_3 for 30 min with occasional shaking. The sample was then separated from acid by decantation and treated with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies.

Distribution Studies

Distribution studies for Pb (II), Bi (III), Th (IV), Zn (II), Mn (II), Cu (II) and Ni (II) ions was carried out by batch method. 100 mg of ZrHEDP was equilibrated with 20 mL of 0.001 M metal ion solution for 24h at room temperature. The metal ion concentration before and after sorption was determined by EDTA titrations (Jeffery, 1978). Distribution studies were also carried out in

different electrolyte media like 0.2 M and 0.02 M NH_4NO_3 , HNO_3 , HClO_4 and CH_3COOH . Distribution coefficient (K_d) was evaluated using the expression, $K_d = [(I-F) \times V] / (F \times W)$ mL. g^{-1} where I is the initial amount of the metal ion in the solution phase, F is the final amount of the metal ion in the solution phase, V is the volume of the metal ion solution (mL) and W is the weight of the ion exchanger.

Binary Metal Separations

For binary separations, 1 g of the ion exchanger was taken in a glass column (30×1.1 cm). The column was washed thoroughly with deionized water and the mixture of the metal ions (1 ml of each metal ion of 0.004 M concentration) to be separated was loaded onto it (flow rate 7-8 drops/minute). The separation was achieved by passing suitable eluant through the column. Metal ion concentration in the effluent was determined quantitatively by AAS (Chemito Model - 201).

Removal of Nickel from an Industrial Effluent

20 mL of industrial effluent containing nickel was shaken with 1 g of exchanger in stoppered conical flasks at different time intervals with increments of 10 min (10, 20, 30, ..., 100). The amount of metal ion remaining was then determined by AAS.

Results and Discussion

ZrHEDP was obtained as colourless transparent granules. Elemental analysis by ICP-AES (Perkin Elmer ICP-AES spectrometer) shows zirconium to phosphorus ratio to be 1:2. The carbon and hydrogen content (Coleman CHN analyzer) were found to be % C = 7.01, % H = 3.21 in ZrHEDP. FTIR spectra of Zr-HEDP (KBr wafer on BOMEM MB) shows broad band in the 3400 cm^{-1} region, attributed to symmetric and asymmetric -OH stretching, while band at 1642 cm^{-1} is attributed to H-O-H bending. This indicates the presence of structural hydroxyl protons in ZrHEDP responsible for cation exchange, which is further evident from the Na^+ i.e.c. value that has been determined. A broad shoulder at 1058 cm^{-1} is attributed to the presence of P=O stretching and bands at 1452 and 1380 cm^{-1} is attributed to symmetric and asymmetric C- CH_3 bending (Silverstein, 1991). The Na^+ ion exchange capacity (i.e.c.), determined by column method (Samuelson, 1953) at room temperature is found to be 3.18 meq g^{-1} . The effect of calcination on i.e.c. was studied in the temperature range 100 to 500°C at an interval of 100°C and found to be 3.20, 3.00, 3.22, 1.96 and 1.55 meq g^{-1} respectively. The initial increase in the i.e.c. value at 100°C could be attributed to loss of

moisture adhered to it, thereby increasing the active exchanger content for same weight of material taken for i.e.c. determination. However, at 300°C an increase in i.e.c. value is observed which is attributed to the decomposition of organic moiety, leading to the formation of active carbon, as evidenced by the change in colour of the heated samples to black. Further, decrease in i.e.c. beyond 300°C is attributed to the complete decomposition of organic moiety/active carbon in the form of CO₂.

TGA of ZrHEDP (Shimadzu Thermal analyzer DT-30 at a heating rate of 10°C/min) exhibits ~11.0% weight loss within the temperature range 40-120°C corresponding to the loss of moisture/hydrated water. A 10.0% weight loss is observed in the range of 220-500°C, which may be due to the condensation of structural hydroxyl groups as well as decomposition and dissociation of the organic moieties. DSC of ZrHEDP (Mettler TA 4000 system at a heating rate of 20°C/min) exhibits endothermic peak at 120°C, which is attributed to loss of moisture/hydrated water. However, an exothermic process starts at 300°C, which is attributed to both decomposition of the organic moiety present in the framework as well as condensation of structural hydroxyl groups. The decomposition of the organic moiety predominates the condensation of structural hydroxyl groups which is observed as an exotherm. Based on the zirconium and phosphorous content determined by ICP-AES, % carbon and % hydrogen as well as thermal analysis (TGA) data, ZrHEDP has been formulated as Zr(C₂H₈P₂O₇) · 2H₂O using Alberti & Torracca formula (Alberti, 1968).

Absence of sharp peaks in X-ray diffractogram of ZrHEDP (X-ray diffractometer BRUCKER AXS D8

using Cu-K_α radiation with a nickel filter) indicates that the material is amorphous in nature. ZrHEDP is stable in acid medium, maximum tolerable limits being 18 M H₂SO₄, 16 M HNO₃, and 11.3 M HCl and also stable in organic solvent media (ethanol, benzene and acetone). It is however not so stable in base medium, maximum tolerable limits being 3 N NaOH and 0.1 N KOH.

The presence of electrolytes in metal ion solution strongly affects the K_d value. When a metal ion pair is to be separated, using a column, the K_d value of a particular metal ion in a particular electrolyte medium is very important as this further gives us a guideline to separate/elute out metal ions using the particular electrolyte. The distribution coefficient (K_d) values evaluated for Zn(II), Cu(II), Ni(II), Pb (II), Bi (III), Th (IV) and Mn (II) has been presented in Table 1. ZrHEDP exhibits good affinity for Pb (II), Zn (II), Mn (II), Cu (II) and Ni (II) as compared to Bi (III) and Th (IV). K_d value of 1760 mL.g⁻¹ for Pb (II) obtained in the present case is higher than obtained for titanium molybdate (1000 mL.g⁻¹) (Qureshi, 1969) and titanium tungstate (1565 mL.g⁻¹) (Chudasama, 1998). Exceptionally high K_d values exhibited by Pb(II) in 0.02 M CH₃COOH (10422.2 mL.g⁻¹) may be due to the formation of lead acetate which is strongly sorbed onto ZrHEDP. Zn (II) and Cu (II) also exhibit exceptionally high K_d value in 0.02 M CH₃COOH whereas Ni (II) exhibits a high K_d value in 0.02 M NH₄NO₃. Higher K_d values in electrolyte media as compared to aqueous media are observed for all metal ions except Mn (II) and Th (IV). This has also been observed earlier by other workers (Sharma, 1994; Varshney, 1990 & 2001).

Table 1: Distribution coefficient (K_d) values of metal ions in aqueous and various electrolyte media on ZrHEDP

<i>Metal ion</i>	<i>Taken as</i>	<i>Distilled water</i>	<i>0.02 M NH₄NO₃</i>	<i>0.2 M NH₄NO₃</i>	<i>0.02 M HNO₃</i>	<i>0.2 M HNO₃</i>	<i>0.02 M HClO₄</i>	<i>0.2 M HClO₄</i>	<i>0.02 M CH₃COOH</i>	<i>0.2 M CH₃COOH</i>
Zn (II)	Acetate	1276	800.00	557.63	1005.82	104.0	593.63	175.10	2300	1123.4
Cu (II)	Sulphate	717.30	872.22	491.56	100.92	437.25	3733.33	1973.68	7025	1549.25
Ni (II)	Acetate	540.66	2433.31	14.14	225.52	1802.0	107.63	20.17	438.92	435.89
Pb (II)	Nitrate	1760	4118.18	201.66	2665.88	334.44	1680	453.66	10422.2	2548.57
Bi (III)	Nitrate	32.96	16.66	38.83	14.29	52.27	29.61	43.26	62.50	51.16
Th (IV)	Nitrate	10.73	8.47	3.89	7.42	10.45	1.97	6.84	2.46	7.48
Mn (II)	Acetate	773.91	52.17	155.15	446.31	22.86	118.86	1.33	511.11	363.55

Based on separation factor α, binary separations for the metal ions pairs, Pb (II) - Th (IV), Pb (II) - Bi (III) and Pb (II) - Ni (II) have been performed (Table 2). In these separations, 0.4 M NH₄NO₃ is used to elute Pb (II), 0.02 M HClO₄ is used for Ni (II) and Th (IV) and 0.02 M HNO₃ is used for Bi (III). The percentage

efficiency of ZrHEDP towards separation of metal ion pairs studied is in the order, Pb (II) (76.31) - Th (IV) (95.72) > Pb (II) (71.13) - Ni (II) (84.79) > Pb (II) (65.82) - Bi (III) (94.58). Though separation factor is very less in case of Pb (II) - Ni (II), the separation is found to be quite efficient.

Table 2: Binary separation of metal ions using ZrHEDP

Separations achieved	$\alpha = K_{d1}/K_{d2}$	Eluant	Metal ion (mg)		Efficiency %
			Loaded	Eluted	
Pb (II) - Th (IV)	164.02	0.02 M HClO ₄ (Th)	0.5282	0.5056	95.72
		0.4 M NH ₄ NO ₃ (Pb)	0.8288	0.6325	76.31
Pb (II) - Bi (III)	53.39	0.02 M HNO ₃ (Bi)	0.4559	0.4312	94.58
		0.4 M NH ₄ NO ₃ (Pb)	0.8288	0.5455	65.82
Pb (II) - Ni (II)	3.25	0.02 M HClO ₄ (Ni)	0.2058	0.1745	84.79
		0.4 M NH ₄ NO ₃ (Pb)	0.8288	0.5896	71.13

Lead and lead compounds are widely used in industry. Lead as a source in water pollution is due to its use in sheet and lead pipe industries, storage batteries, paints and pigments, pesticides, preparation of alloys etc. The biochemical effects of lead is well known and described in texts (De, 1987; Wright, 2002). The most promising property of the material ZrHEDP is its high selectivity for lead. An extremely high affinity of Pb (II) towards ZrHEDP suggests its possible use for removal of lead as well as its separation from other metal pollutants.

Nickel and its salts find applications in electroplating industries, storage batteries, catalyst industry, alloys (stainless steel manufacture), paints and pigments etc. Ni (II) in the divalent state is highly soluble in water. The biochemical effects of nickel is well known and described in texts (De, 1987 Wright, 2002). ZrHEDP was used to remove nickel from an industrial effluent containing nickel with initial concentration 237.5 mg.L⁻¹. The effluent has been obtained from a catalyst based industry, which uses a nickel-supported catalyst. Leaching of Nickel takes place during its use as a catalyst which we have tried to identify/recover using ZrHEDP. It is observed that sorption increases gradually with increase in contact time and reaches a maximum value. Percentage uptake with 10 mins intervals was found to be 42.20 (10 mins), 78.95 (20 mins), 84.21 (30 mins), 89.47 (40 mins) and 89.89 (50 mins).

Conclusion

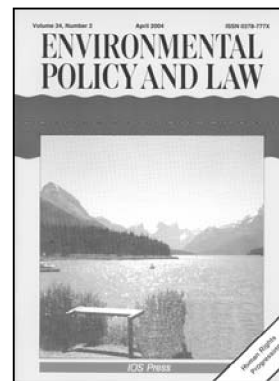
ZrHEDP exhibits the characteristics of a promising ion exchanger, the most promising property being its high selectivity for lead, suggesting its use for removal of lead as well as its separation from other metal pollutants. Its analytical importance has been demonstrated by separating several metal ion pairs.

References

- Alberti, G., Constantino, U., Alluli, S. and M. Tomassini (1978). Crystalline Zr(RPO₃)₂ and Zr(R-OPO₃)₂ compounds (R=Organic radical): A new class of materials having layered structure of zirconium phosphate type. *J. Inorg. Chem.*, **40**: 1113-1117.
- Alberti, G. and U. Costantino (1996). Comprehensive Supramolecular Chemistry. Pergamon-Elsevier Science Ltd., London (Eds).
- Alberti, G. and E. Torracca (1968). Crystalline insoluble acid salts of polyvalent metals and polybasic Acids -VI Preparation and ion exchange properties of crystalline titanium arsenate. *J Inorg Nucl Chem.*, **30**: 3075-3080.
- Chudasama, U. and B. Pandit (1998). *Ind J Chem*, **37A**: 931.
- Clearfield, A. (1998). Progress in Inorganic Chemistry. John Wiley and Sons, New York, Vol 47: 371.
- Clearfield, A., Zhang, B., Poojary, D.M. and G.Z. Peng (1996). Synthesis, Characterization, and Amine Intercalation Behavior of Zirconium *N*-(Phosphonomethyl)iminodiacetic Acid Layered. *Chem Mater*, **8**: 1333-1340.
- De, A.K. (1987). Environmental Chemistry; Wiley Eastern Limited: Delhi. 62-63.
- Jeffery, G.H., Bassett, J., Mendham, J. and R.C. Denney (1978). Vogel's Text Book of Quantitative Inorganic Analysis, 5th ed. Longman Green London, 324 - 325.
- Mar Gómez-Alcántara, M., Aurelio Cabeza, María Martínez-Lara, Miguel, A.G., Rafael, S., Bhuvanesh, N. and A. Clearfield (2004). Synthesis and Characterization of a New Bisphosphonic Acid and Several Metal Hybrids Derivatives. *Inorg Chem.*, **43**: 5283-5293.
- Qureshi, M. and H.S. Rathore (1969). *J Chem Soc (A)*, 2515.
- Samuelson, O. (1952). Ion exchangers in Analytical Chemistry. John Wiley & Sons, New York.
- Sharma, S.D., Misra, S. and A. Agrawal (1994). *Indian J Chem.I*, **33 A**: 696.
- Silverstein, R.M., Bassler, G.C. and T.C. Morill (1991). Spectrometric identification of organic compounds, 5th ed. John Wiley and Sons, New York.

- Takahashi, H. and Oi. T. Hosoe (2002). Characterization of semi crystalline titanium phosphates and their selectivity of cations and lithium isotopes. *J. Mater. Chem.*, **12**: 2513-2518.
- Varshney, K.G. and U. Gupta (1990). Tin(IV) Antimonate as a Lead-Selective Cation Exchanger: Synthesis, Characterization, and Analytical Applications. *Bull Chem Soc Japan*, **63**: 1515-1520.
- Varshney, K.G., Tayal, M., Khan A.A. and R. Niwas (2001). *Coll and Surf (A)*, **181**: 123.
- Varshney, K.G. and A.M. Khan (1995). Inorganic ion exchanger in Chemical Analysis. Qureshi M. and K.G. Varshney (eds). CRC Press Inc., Boca Raton, Florida, p.177.
- Wright, A.D. and P. Welbourn (2002). Environmental Chemistry. Cambridge University Press, UK. 287-288.

Environmental Policy and Law



Aims and Scope

This international journal is created to encourage the exchange of information and experience on all legal, administrative and policy matters relevant to the human and natural environment in its widest sense: air, water and soil pollution as well as waste management; the conservation of flora and fauna; protected areas and land-use control; development and conservation of the world's non-renewable resources. In short, all aspects included in the concept of sustainable development. For more than two decades *Environmental Policy and Law* has assumed the role of the leading international forum for policy and legal matters relevant to this field. *Environmental Policy and Law* is divided into sections for easy accessibility. These sections cover the activities of the United Nations and its specialized agencies, other international developments, regional activities within the framework of European Union, AU, ASEAN, etc., and developments at the national level from all over the world. An important and distinctive feature is the publication of selected documents appearing with the minimum of delay, which are not easily accessible, such as the resolutions from non-public meetings of parliamentarians, guidelines or draft conventions not yet published or newly concluded agreements. *Environmental Policy and Law* fills a gap left by other publications.

Subscribers are politicians, government officials at the highest level of decision-making, academics, scientists, practicing lawyers, firms, and private persons wishing to keep up to date on contemporary policies and practices.

Editor-in-Chief

Dr. Wolfgang E. Burhenne
c/o International Council of Environmental Law
Godesberger Allee 108-112
D-53175 Bonn
Germany
Tel.: +49 228 26 92 240
Fax: +49 228 26 92 251/252
Email: icel@intlwapol.org

Subscription Information 2009

ISSN 0378-777x
1 volume, 6 issues (Volume 39)
Institutional subscription (print and online):
€537 / US\$777 (including postage and handling)
Institutional subscription (online only):
€480 / US\$695

Receive the journal on a regular basis to keep up-to-date on the newest information in your field of expertise. As a subscriber to this IOS journal you can get free electronic access with a print subscription. You can also choose to sign up for the electronic version without paying for postage and handling.

IOS Press is a rapidly expanding Scientific, Technical, Medical and Professional publishing house focusing on a broad range of subject areas, such as; medical science, healthcare, telecommunication, artificial intelligence, information and computer science, parallel computing, physics and chemistry, environmental science, and other subjects.

IOS
Press

IOS Press
Nieuwe Hemweg 6B
1013 BG Amsterdam
The Netherlands
Tel.: + 31 20 688 3355
Fax: + 31 20 687 0039
Email: market@iospress.nl
URL: www.iospress.nl

IOS Press, Inc.
4502 Rachael Manor Drive
Fairfax, VA 22032, USA
Tel. +1 703 323 5600
Fax: +1 703 323 3668
Email: sales@iospress.com