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The solubilities of the alkali metal salts and the precipitation of Cs^+ from aqueous solution

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Contents

Abstract

Radioactive ^{137}Cs may be removed from nuclear waste aqueous solutions by precipitation. Alkali metal salt solubility trends show that the Cs^+ salts have the largest range of solubilities for all of the alkali metal salts and that Cs^+ should be the most likely ion of the group to form a precipitate in solution. The tetraphenylborate anion ($B(C_5H_5)_4^-$, TPB) precipitates Cs^+ as the insoluble CsTPB. However, there are a number of problems associated with this compound and another precipitating agent is needed. A potential substitute is the cobalt dicarbollide anion ($Co(B_9C_2H_{11})_2^-$, CDC) which forms a slightly more soluble compound, CsCDC. The anion:cation volume ratios for several simple alkali metal salts, when compared with their solubility values, indicate that forces within the solid crystal control solubility. Similar comparisons for the TPB and CDC anions indicate that the solubilities are controlled by the hydrophobic nature of the anion. Some requirements are proposed for an anion to form a precipitate with Cs^+.

Keywords: ^{137}Cs; Alkali metal salts; Solubilities; Aqueous solution

1. Introduction

The removal and isolation of radioactive nuclear waste components from the environment are important concerns [1]. One component, ^{137}Cs, is especially hazard-

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ous [2], for it has been difficult to remove from aqueous solution. This isotope, a β emitter, is a radioactive fission product with a half-life of about 30 years. It is in the solution phase of the waste, usually with significant amounts of inactive Na^+ and K^+ ions. Thus, separation of relatively small amounts of Cs^+ from large amounts of Na^+ and K^+ is necessary.

Precipitation, ion exchange and extraction into an organic solvent are three methods to remove metal ions from aqueous solution. They are common methods to remove transition and alkaline earth metals from aqueous solution. A wide variety of precipitating and extraction agents are available to separate closely related metals. Unfortunately, most of these agents are ineffective in precipitating or extracting alkali metal ions from solution. Precipitation is especially difficult since most alkali metal salts usually are very water soluble.

The Savannah River Site (SRS) has in storage over 30 million gallons of nuclear waste from which the highly radioactive components are eventually to be removed and mixed with borosilicate frit [3,4]. This mixture is then to be vitrified, and the radioactive glass matrix isolated in an underground repository. The solid phase of the waste slurry, now in storage, consists primarily of heavy metal hydroxides and oxides, while the solution phase is highly basic ($pH \approx 14$) with high concentrations of Na^+ (≈ 5 M) and K^+ (≈ 0.1 M). A major radioactive species in solution is ^{137}Cs at a concentration level of approximately 0.1 mM. At this time ^{137}Cs is to be precipitated with sodium tetraphenylborate, NaTPB, and the solid CsTPB stored [5] before being added to the stream going to the vitrification process. However, there are problems with this proposal that will be discussed below.

Extraction and ion exchange are being used, or being considered for use, in separating and isolating ^{137}Cs from acidic aqueous waste solution, and these topics have been reviewed [1] and treated recently [6]. This review will examine only precipitation. The general nature of the solubility of alkali metal compounds will be examined, and some specific reagents for Cs^+ precipitation described. Some characteristics of potential Cs precipitating agents will be proposed.

2. Alkali metal salt solubilities

The aqueous solubilities of a large number of alkali metal compounds are available in compilations such as Lange's Handbook [7]. Listed in Lange's Tables 4-1 and 10-2 are the solubilities of 31 Cs^+ salts, 31 K^+ salts and 31 Na^+ salts with each group having the same set of anions. The solubilities of 28 Rb^+ salts and 24 Li^+ salts are also listed with each salt having one of the 31 anions. By comparing the values, it was possible to develop some general relationships about alkali metal salt solubilities that cover a wide range of anion types, including tetrahedral, octahedral, univalent, divalent, organic, and complex oxo anions. Table 1 summarizes the data found in Lange's Handbook. The Cs compounds showed the widest range of solubilities from Cs_2PtCl_6, with a solubility at 20 °C of 1.6×10^{-4} molal, to $CsC_2H_3O_2$, with a 20 °C solubility of 52.7 molal, giving a ratio of solubilities of the most soluble salt

Table 1
Solubility ranges for alkali metal salts listed in Lange's Handbook (Ref. [7])

Least soluble	Most soluble	Solubility range[a]	Low solubility fraction[b]
Cs_2PtCl_6	$CsC_2H_3O_2$	3×10^5	14/31
Rb_2PtCl_6	$RbCHO_2$	9×10^4	12/28
K_2SiF_6	$KCHO_2$	6×10^3	14/31
$Na_2C_2O_4$	$NaOH$	1×10^2	6/31
LiF	$LiClO_3$	8×10^2	2/24

[a] Solubility of most soluble salt divided by that of the least soluble salt.

[b] Numerator is the number of compounds with the solubility equal to 1 molal or less; denominator is the total number of compounds.

to the least soluble salt of approximately 3×10^5. The Na^+ salts had the smallest range with a solubility ratio of about 1×10^2. About half of the Cs^+ compounds have solubilities less than 1 molal, while the Li^+ compounds have only 2 (LiF and LiC_2O_4) out of 24 with relatively low solubilities. Therefore, the most likely candidate of the group for aqueous precipitation is Cs^+.

Anions that have a Cs^+ salt with relatively low solubility ($PtCl_6^{2-}$, MnO_4^-, $Al(SO_4)_2^-$, SiF_6^{2-}, $AuCl_4^-$ and I^-) show a trend of increasing solubility with decreasing atomic number, i.e. $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$, while the most soluble Cs^+ salts have anions (CrO_4^{2-} and OH^-) which show the reverse trend. Many of the other anions have the Na^+ or K^+ compound significantly more insoluble or soluble than the Li^+ or Cs^+ compounds. (See Table 2 for some examples.)

A thermodynamic cycle may explain the solubility behavior of these salts [8]. For dissolving a 1:1 salt, MX, in water, the salt crystal converts to gaseous ions, $M^+(g)$ and $X^-(g)$, which involves the MX lattice energy. Then, the gaseous ions when placed into water form $M^+(aq)$ and $X^-(aq)$, generating hydration energy. If the lattice energy is large or the hydration energy small, then the overall energy for the solubility process would be small and unfavorable. Therefore, low salt solubility may result from strong forces within the solute crystal or low attraction of water molecules for the solute ions, or both.

Considerable attention has been focused recently on the relation between the size and shape of inorganic molecular ions and their relevance to crystallization problems [9,10]. Ion volumes have been calculated from crystal structure data and then related to crystallization. The ratio V_a/V_c of the anion volume to cation volume is a factor that makes it possible to compare the crystallization behaviors of a wide range of salts. This ratio has not been used to examine the solubilities of simple salts, and it might enable the development of some generalizations about their solubilities.

The solubilities of the Cs^+, Rb^+, K^+, Na^+ and Li^+ perchlorates, nitrates, iodides, bromides, chlorides and fluorides are listed in Table 2 along with the anion:cation volume ratios. The volumes of the monatomic ions, Cs^+, K^+, Na^+ and Li^+, along with those of ClO_4^- and NO_3^- were obtained from recent calculations [9], while

Table 2
Molal solubilities of selected alkali metal salts related to ion volumes

Anion	T (°C)	Solubility	Ref.	Volume ratio[a]
Cesium ($V_{cation} = 19$ Å^3 (20.2 Å^3))[b]				
ClO_4	25	0.088	[11]	2.5
NO_3	20	1.18	[12]	1.8
I	20	2.94	[7, p. 4–40]	2.2
Br	25	5.80	[13]	1.6
Cl	25	11.3	[13]	1.3
F	18	24.2	[13]	0.55
Rubidium ($V_{cation} = 13.6$ Å^3)[b]				
ClO_4	25	0.097	[14]	3.5
NO_3	20	7.65	[7, p. 4–101]	2.5
I	25	7.70	[15]	3.1
Br	25	7.01	[15]	2.3
Cl	25	7.80	[15]	1.8
F	18	28.8	[13]	0.77
Potassium ($V_{cation} = 10$ Å^3 (9.9 Å^3))[b]				
ClO_4	25	0.147	[16]	4.7
NO_3	25	2.70	[12]	3.4
I	25	8.94	[17]	4.2
Br	25	5.73	[16]	3.1
Cl	25	4.81	[18]	2.5
F	25	17.5	[16]	1.1
Sodium ($V_{cation} = 3$ Å^3 (3.6 Å^3))[b]				
ClO_4	25	17.2	[19]	16
NO_3	25	10.7	[16]	11
I	25	12.3	[16]	14
Br	25	9.20	[16]	10
Cl	25	6.16	[16]	8.3
F	25	0.989	[16]	3.5
Lithium ($V_{cation} = 2$ Å^3 (0.9 Å^3))[b]				
ClO_4	25	5.63	[20]	24
NO_3	25	10.9	[21]	17
I	25	12.5	[22]	21
Br	25	19.6	[23]	16
Cl	20	20.0	[16]	12
F	25	0.051	[24]	5.2

[a] Volume ratio: V_{anion}/V_{cation}. Volumes of anions calculated from Pauling ionic radii are as follows: F^-, 11 Å^3; Cl^-, 25 Å^3; Br^-, 31 Å^3; I^-, 42 Å^3. The volumes of anions from Ref. [9] are as follows: NO_3^-, 34 Å^3; ClO_4^-, 47 Å^3.

[b] The cation volume is from Ref. [9]. The values in parentheses are calculated from Pauling ionic radii [25]. There was no value for Rb^+ in Ref. [9].

that of Rb^+ was calculated from the ionic radius [25]. The volumes of the other cations calculated from the ionic radii are included for comparison. Fig. 1 shows a plot of ln(molal solubility) vs. V_a/V_c for the compounds given in Table 2.

Except for Li^+, the ion volumes calculated from ionic radii and those from the recent literature compare well. The Li compound solubilities seem to fit better with the other solubility values when compared using the Mingos and Rohl [9] value.

The ln(molal solubility) vs. V_a/V_c curve has an interesting shape. At low values of the ratio ln(molal solubility) decreases with the low point of the curve around 2.5–3.5 and then increases. At the minimum, where compounds with maximum insolubility are found, there is considerable scatter of the values. Specific interactions for the ions and activity corrections might lead to this scatter.

A volume ratio of 3 would give, assuming a spherical shape of both ions, a cation:anion radius ratio of 0.69. This is close to the value (0.75) shown by Pauling [26] that is expected for minimum interelectronic repulsion and maximum crystal energy for the alkali halide (NaCl) lattice. This indicates for these salts that the solubility relationships are governed primarily by forces within the crystalline solid and less by hydration interactions. This may not be the case for other types of alkali metal salt solubilities as discussed in the next section.

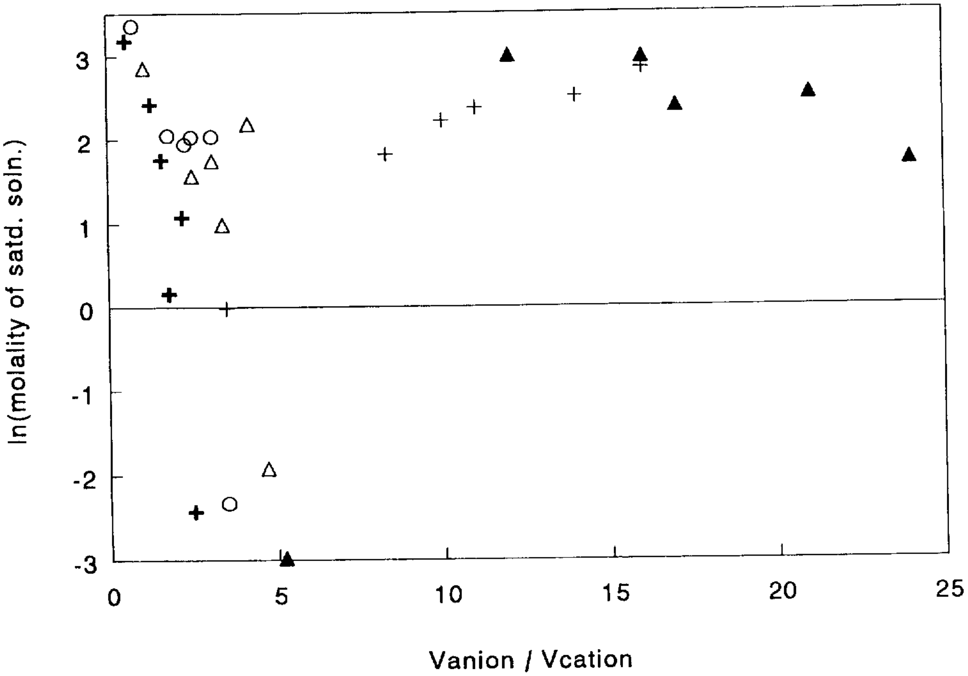

Fig. 1. The logarithm of the molal solubility of certain alkali metal salts vs. the volume ratio for the anion to cation: ✚, Cs; ○, Rb; △, K; +, Na; ▲, Li. The symbols in a given metal series are from left to right F, Cl, Br, NO_3, I, ClO_4.

3. The solubility of some cesium salts

The crystal structures of several 1:1 cesium salts with known solubilities are in the literature. Using the reported cell volumes and the volume of the Cs^+ ion (19 Å^3), the anion volumes may be calculated with the packing coefficient (Eq. (1)). The packing coefficient C_k relates the cation and anion volumes to the cell volume. Eq. (1) defines C_k for ionic salts [10]:

$$C_k = Z[(n_a V_a + n_c V_c)/V_{cell}] \times 100\% \tag{1}$$

where Z is the number of formula units per unit cell, n_a is the number of anions and n_c the number of cations per formula unit, V_a is the volume of the anion, V_c, the volume of the cation and V_{cell} the volume of the unit cell. After examining a number of representative crystal structures, it was found that the best estimate of C_k for a 1:1 salt composed of spherical ions is 68.9%. Knowing the volume of one ion and having both ions of comparable size, the volume of the other ion may be calculated with an accuracy of 10%.

The anion volumes and the corresponding Cs salt solubilities are presented in Table 3. Because of the restrictions on Eq. (1), the calculated volumes are approximate. However, the values do show that as the anion volume increases the solubility decreases.

Two Cs salts that are insoluble in water, cesium tetraphenylborate, $Cs^+[B(C_6H_5)_4]^-$ (CsTPB), and cesium cobaltdicarbollide, $Cs^+[Co(B_9C_2H_{11})_2]^-$ (CsCDC), have different volume relationships than the salts discussed in the above section. CsTPB is less soluble than Cs_2PtCl_6, the most insoluble Cs compound found in Lange's Handbook [7], and CsCDC is slightly more soluble than Cs_2PtCl_6. CsTPB has a solubility of 2.8×10^{-5} M at 20 °C, while the KTPB solubility is 1.45×10^{-4} M and NaTPB is very soluble [27]. CsCDC has an ambient temperature solubility of 1×10^{-3} M [28], while those of KCDC and NaCDC are approximately 0.5 M and 1.0 M respectively [50]. The hexabromo analog, $CsCo(B_9C_2H_8Br_3)_2$ ($CsCDCBr_6$), is even more insoluble, with a reported solubility of 0.3 mM in water at ambient temperature [28]. (A review of the chemistry of CDC has recently been published [51].)

The volume of the TPB anion has been reported [9] to be 323 Å^3, while that for the CDC anion may be calculated from the CsCDC structure [30]. From the unit cell volume for CsCDC, 1792 Å^3, the approximate CDC anion volume is 290 Å^3. The V_a/V_c ratios for TPB are then 17 (Cs), 32 (K), and 108 (Na), while those for CDC are 15 (Cs), 29 (K), and 97 (Na). All of the ratios are probably much larger than those for most alkali metal salts because of the large sizes of the two anions. CsTPB and CsCDC have very negative ln (molal solubility) values with large values of V_a/V_c. The data for the two insoluble salts do not fit the pattern shown by the compounds in Fig. 1 which is probably due to the hydrophobic nature of the anions.

The hydrophobicity of the anions would be characterized by a small charge density ratio, the −1 charge divided by the volume, wherein the small charge is spread out over a large volume. A lack of polar character and relatively high symmetry within

Table 3
Relation of solubilities of Cs^+ 1:1 salts with volume of −1 anions

Anion	Solubility[a]	T (°C)[b]	Ref.	Anion volume (Å^3)	Ref.
$B(C_6H_5)_4$	2.8×10^{-5} M	20	[27]	323	[9]
$Co(B_9C_2H_8Br_3)_2$	3×10^{-4} M	AT	[28]	404	[29]
$Co(B_9C_2H_{11})_2$	9.8×10^{-4} M	AT	[28]	285	[30]
MnO_4	0.0091 M	19	[31]	61	[32]
$Al(SO_4)_2$	0.014	25	[12]	100	[33]
$AuCl_4$	0.017	20	[34]	46	[35]
IO_4	0.066	15	[36]	68	[37]
BF_4	0.075	20	[38]	38	[9]
ClO_4	0.088	25	[11]	47	[9]
IO_3	0.084	24	[36]	51	[39]
BrO_3	0.14	25	[40]	51	[41]
$C_4H_5O_6$[c]	0.25 M	20	[11]	105	[42]
ClO_3	0.29	25	[14]	49	[43]
NO_3	1.18	20	[12]	34	[9]
I	2.94	20	[7, p. 4–40]	42	[25]
Br	5.80	25	[13]	31	[25]
Cl	11.3	25	[13]	25	[25]
N_3	17.6	16	[44]	41	[45]
F	21.2	18	[13]	11	[25]
OH	25.7	15	[46]	22	[47]
$C_2H_3O_2$	53.1	21.5	[48]	49	[49]

[a] Molal solubility unless otherwise indicated.
[b] AT, ambient temperature.
[c] The anion $C_4H_5O_6^-$ is the acid tartrate species.

the species is no doubt important to keep the charge spread as evenly as possible over the anion. This would be expected to minimize the interaction of water molecules in solution with the anions and to promote low solubility with the large cation.

The solubilities of certain Cs tetraphenylborate derivatives were examined by Moore and co-workers in the late 1960s in order to find an analytical reagent that might quantitatively precipitate K, Rb, Cs, protonated basic nitrogen, and quaternary ammonium salts and have a greater stability in solution than TPB [52–55]. The solubilities of several of the alkali metal salts were measured and are given in Table 4. The derivative salts all have a somewhat greater solubility than the TPB salt, possibly because of the −1 charge being unevenly distributed in the derivatized anion.

4. The requirements for a cesium precipitating agent

As mentioned, NaTPB is being considered as the precipitating agent for ^{137}Cs from nuclear waste at the SRS. When this compound is used to precipitate Cs, not only does CsTPB precipitate, but also considerable amounts of KTPB as well,

Table 4
Molar solubilities of certain alkali metal tetraphenylborate salts ($M^+[B(C_6H_4X)_4^-]$)

M	X	T (°C)	pH of solution	Solubility (mM)	Ref.
Cs	H	20	Water	0.028	[27]
Cs	*p*-F	25	7.2	0.46	[53]
Cs	*m*-F	25	6.5	0.12	[54]
Cs	*m*-CF_3	25	6.5	0.18	[55]
K	H	20	Water	0.145	[27]
K	*p*-Cl	25	6.7	0.65	[52]
K	*m*-F	25	6.7	1.41	[54]
K	*p*-CF_3	25	6.3	0.27	[54]
Rb	*m*-F	25	6.4	0.35	[54]

requiring much more precipitating agent than necessary. While in storage, the radioactivity present causes radiolytic decomposition of the TPB anion to produce primarily environmentally harmful benzene [5,56]. The high carbon content of CsTPB makes it necessary to hydrolyze the precipitate, using a complex procedure, prior to the incorporation of ^{137}Cs into the glass matrix. The large amount of carbon would create too much of a reducing environment in the glass formation process, producing an inferior product. It would be much more advantageous to be able to add a Cs precipitate directly to the glass-forming mixture with little or no prior treatment. Because of these problems an alternative to TPB precipitation is needed.

In order to obtain the reaction

$$m\mathrm{Cs}^+(\mathrm{aq}) + \mathrm{M}_m[\mathrm{AX}_n] \rightarrow \mathrm{Cs}_m[\mathrm{AX}_n](\mathrm{s}) + m\mathrm{M}^+(\mathrm{aq})$$

using as a precipitating agent the complex ion $[AX_n]^{m-}$ some requirements might be proposed. After considering the solubility relationships of the Cs compounds, it was found that $[AX_n]^{m-}$ should have the following in order to precipitate Cs^+: (a) -1 charge; (b) hydrophobic character; (c) relatively high symmetry; (d) volume of approximately 300 Å^3; (e) weak base character. Then, in order to serve as an ideal precipitating agent for the radioactive Cs in a large-scale process, the anion should also (a) be chemically inert, i.e. compatible with nuclear waste, (b) produce a precipitate with a high percentage of Cs, (c) generate a solubility order of $\mathrm{Na} \approx \mathrm{K} \gg \mathrm{Cs}$, and (d) be easy and inexpensive to prepare and/or obtain.

If X is a formally monovalent species, such as phenyl, then in order to have $m=1$ the oxidation state of A would have to be III for a tetrahedral structure ($n=4$), as for the boron atom in TPB, or V for an octahedral structure ($n=6$). If X is a divalent species, such as an oxide, then in order to have $m=1$ the oxidation state of A would have to be VII as for a tetrahedral structure, e.g. ClO_4^-. The central atom, A, probably cannot be a low oxidation state metal ion since such complexes would no doubt hydrolyze in base solution. A high oxidation state metal ion would be expected for A, but this species probably would be a good oxidizing agent. Second- and third-row transition metals might be considered in order to have relatively inert tetrahedral or octahedral complexes; however, the majority of them are prohibitively expensive. Most AX_n^- anions may be ruled out as precipitating species.

The anion $PtCl_6^{2-}$ cannot be considered for Cs precipitation because of its high cost. Other anions similar to it probably would be as expensive. More hydrophilic anions that might form strong crystal bonds do not appear to offer a wide range of preparative possibilities as do the hydrophobic cage structures. One difficulty found with the derivatized TPB anions is that the Na salt of such an anion is often less soluble than NaTPB.

The CDC anion is unique with two boron hydride cages ($B_9C_2H_{11}^-$) bound to a Co(III) central atom in a dumb-bell shape manner. There are many other examples of large −1 boron hydride cage anions (all eight articles in Ref. [57] are devoted to B chemistry and show a wide range of B–H cages). Many of these were originally isolated as the Cs salt and might serve to precipitate Cs very effectively. They need to be examined further as potential Cs precipitating agents.

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