Principle of Common-ion Effect and its Application in Chemistry: a Review

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\begin{abstract}
Common-ion effect is a shift in chemical equilibrium, which affects solubility of solutes in a reacting system. The phenomenon is an application of Le-Chatelier’s principle for equilibrium reactions that has become a regular occurrence in chemistry analysis and industrial researches. It is an important phenomenon that can be used in practice, to understand some reaction conditions that could favour an increased product formation. In Chemistry, its principle is thought to rely on its ability to exploit the availability of an ion present in each of the reacting compounds in a reacting system to suppress the solubility of one of the ionic substances upon contact with another ionic compound. Due to the precipitating effect of the presence of common-ions in equilibrium solutions, the common-ion effect is considered one of the factors that affect the solubility of a compound. The principle of common-ion effect applies in many chemical processes including those involved in buffering solutions, purification of salts, salting out of soap, precipitation of salts, manufacture of baking soda, water treatment and are frequently applied in many manufacturing industries including the pharmaceutical industries. In this paper, we performed a concise updated desk literature review on the principle of Common-ion effect with the view to provide a greater understanding of the concept and its importance in chemistry.

\textbf{Keywords:} Equilibrium reaction, Ionic substances, Solubility, Product formation, Precipitation
\end{abstract}

1. Introduction

The effect of common-ions in equilibrium solutions is an important and interesting aspect in chemistry and other studies relating to chemical equilibrium. The common-ion effect is a term used to refer to the decrease in the solubility of a salt that occurs when the salt is dissolved in a solution that contains another source of one of its ions [1]. It is a regular occurrence in chemical analysis and plays significant role on solubility and the dissolution rate of salts. It is also described as a phenomenon in which the degree of dissociation of any weak electrolyte can be suppressed by adding a small amount of strong electrolyte containing a common-ion [2]. The concept describes a shift in equilibrium caused by the addition or removal of one of the compounds, which takes part in the equilibrium [3]. The presence of Common-ion generally affects the solubility of salts and other weak electrolytes because it basically decreases the solubility of a solute as the ionization of a weak acid or weak base is decreased by any strong electrolyte that provides a common ion [4]. And since the solubility of solids that contain common ions with solvent is lower than solubility in pure solvents [4], Silver trioxonitrate (iv) AgNO\textsubscript{3} salt for instance, is said to be more soluble in pure water than it is in Sodium trioxonitrate (iv) NaNO\textsubscript{3} because they have the nitrate ion (NO\textsubscript{3}\textsuperscript{-}) in common.

However, this effect cannot be observed in the compounds of transition metals as they have a tendency to form complex ions [5]. But it can be observed in the compounds insoluble in water. This is because the addition of a common-ion can prevent the ionization of the weak acid or weak base as much as it would without the added common ion. Furthermore, common-ion effect can be observed in such reactions involving the decrease in the solubility of the salt in a solution that already contains an ion common to that salt [5].

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Solubility of salts is influenced by several factors including temperature, presence of a common ion, salt effect, pH of solution and presence of complexing agents [6]. In his studies, Tosh [7] had showed that solubility generally increases with increased temperature; presence of common ions reduces solubility; salt effect slightly increases solubility; pH of solution affects the solubility of ionic compounds in which the anions are conjugate bases of weak acids; whereas formation of complex ion increases solubility.

The common-ion effect is an application of Le-Chatelier’s principle, which states that when a system in dynamic equilibrium is acted upon by an external stress, it will adjust in such a way as to relieve the stress and establish a new equilibrium [8]. If a common ion is added to a weak acid or weak base equilibrium, the equilibrium will shift towards the reactants (the weak acid or base), in order to restore the balance. It also can have an effect on buffering solutions as adding more conjugate ions may shift the pH of the solution.

In a saturated solution, if the concentration of any one of the ions is decreased, following the Le-Chatelier’s principle, more salt dissolves, and the equilibrium shifts towards the right, until the solubility product constant equals the product constant $K_{sp}$ = $Q_{sp}$ [9]. In addition, if the concentration of any one of the ions is increased by adding an electrolyte, the equilibrium shifts towards the left according to the Le-Chatelier’s principle, until $K_{sp}$ = $Q_{sp}$. In practice, the dissociation of a weak electrolyte is decreased by adding to the solution, a strong electrolyte or salt, which has an ion in common with the weak electrolyte. The common-ion effect is often used to completely precipitate any one of the ions as its sparingly soluble salt with a very low value of solubility product for gravimetric estimation [9].

According to Le-Chatelier’s principle, when a system is in equilibrium, addition of additional reactant or reduction in the concentration of any product shifts the equilibrium to the right, towards the side of the products. Whereas, the equilibrium shifts to the left upon the addition of an additional product to a reacting system or removal of reactants from the reacting system, in order to produce more reactants [10]. Thus, according to Le-Chatelier’s principle, reversible reactions are self-correcting; whenever these types of reactions are thrown out of balance by a change in concentration, temperature, or pressure; the system will naturally shift in such a way as to re-balance itself after the change.

The common-ion effect plays important roles in controlling the pH of a solution, determining the solubility of a slightly soluble salt and thus can control the formation of a precipitate by either reversing the dissociation of the acid, if the acid had already dissociated or reducing the dissociation [10] if the salt is added first. In this research, we examine the phenomenon of common ion effect as a strong factor affecting solubility of ionic compounds, specifically highlighting its principle, with emphasis on the various reactions where the phenomenon is often encountered.

2.0. Illustrations of the Common-ion Effect

Common-ion effect can be illustrated in the reactions between Ammonium hydroxide (NH₄OH) and Ammonium chloride (NH₄Cl) whereby the ammonium chloride suppresses the ionization of ammonium hydroxide leading to decrease in the hydroxide ion concentration and an increase in the hydrogen ion concentration with subsequent decrease in the pH value of solution [10]. Some common ions of importance in Chemistry have been previously reported (Table 1.) [11].

The phenomenon of common-ion effect occurs in the reactions involving the following species: Ethanoic acid (CH₃COOH) and Sodium ethanoate (CH₃COONa) [12]; Silver tetraoxosulphate (vi) acid (Ag₂SO₄) and Sodium tetraoxosulphate (vi) acid (Na₂SO₄) [13]; Sodium chloride (NaCl) and a solution of hydrochloric acid in water (HCl + H₂O) [14]; Potassium trioxocarbonate (iv) (K₂CO₃) and Magnesium trioxocarbonate IV (Mg₃(CO₃)₂) [15]; Barium trioxonitrate (iv) (Ba(NO₃)₂) and Barium trioxonitrate (iv) (Ba(NO₃)₂) [3]; Barium tetraoxosulphate (vi) (BaSO₄) and Sodium tetraoxosulphate (vi) acid (Na₂SO₄) [3]; Sodium fluoride (NaF) and Calcium fluoride (CaF₂) [5].

<table>
<thead>
<tr>
<th>Cations</th>
<th>Anions</th>
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<tbody>
<tr>
<td>Aluminum</td>
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<tr>
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<td>Ca²⁺</td>
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<tr>
<td>Copper</td>
<td>Cu²⁺</td>
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<tr>
<td>Hydrogen</td>
<td>H⁺</td>
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<tr>
<td>Iron (II)</td>
<td>Fe²⁺</td>
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<tr>
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<td>Fe³⁺</td>
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<tr>
<td>Magnesium</td>
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<td>Mercury (II)</td>
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<td>Ammonium</td>
<td>NH₄⁺</td>
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<tr>
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<td>Mercury (I)</td>
<td>Hg²⁺</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba²⁺</td>
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</tbody>
</table>

Table 1. Common ions and their symbols.
2.1. Dissociation of a weak acid

Ionization of weak electrolyte, ethanoic acid (CH3COOH) is suppressed upon addition of a strong electrolyte, sodium ethanoate (CH3COONa) which has ethanoate ion (CH3COO-) in common. Normally, addition of water to an electrolyte, ethanoic acid (CH3COOH) will cause the dissociation of the electrolyte [13].

\[
\text{CH}_3\text{COOH}_{(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-_{(aq)} + \text{H}^+_{(aq)}.
\]

However, addition of small amount of a strong electrolyte such as sodium ethanoate (CH3COONa) to the aqueous solution of the ethanoic acid (CH3COOH), ultimately results in the dissociation of the former.

\[
\text{CH}_3\text{COONa}_{(aq)} \rightarrow \text{CH}_3\text{COO}^-_{(aq)} + \text{Na}^+_{(aq)}.
\]

From the above, it follows that, the ethanoate ions (CH3COO-) are common in the preparation so, their concentration in the solution will increase. According to Le-Chatelier’s principle, equilibrium shifts towards the left until \(K_{sp} = Q_{sp}\). In order to keep the value of dissociation constant of the acid \((K_a)\) constant, the concentration of ethanoic acid (CH3COOH) molecules is increased so that the addition of sodium ethanoate (CH3COONa) suppresses the ionization of ethanoic acid (CH3COOH) and eventually increases the pH of the solution [13].

2.2. Dissociation of a weak base

Ionization of weak electrolyte, ammonium hydroxide (NH4OH) is suppressed when a strong electrolyte, ammonium chloride (NH4Cl) which has ammonium ion (NH4+) in common is added. Following previous conditions, the addition of water to an electrolyte, ammonium hydroxide (NH4OH) will cause the dissociation of the electrolyte [14].

\[
\text{NH}_4\text{OH}_{(aq)} \rightleftharpoons \text{NH}_4^+_{(aq)} + \text{OH}^-_{(aq)}.
\]

But, addition of a small amount of a strong electrolyte like ammonium chloride (NH4Cl) to the aqueous solution of the ammonium hydroxide (NH4OH), will lead to the dissociation of the ammonium chloride.

\[
\text{NH}_4\text{Cl}_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{Cl}^-_{(aq)}.
\]

In the same order, the ammonium ions (NH4+) are common; hence, their concentration in the solution will increase. According to Le-Chatelier’s principle, equilibrium will shift towards the left until \(K_{sp} = Q_{sp}\). And to keep the value of dissociation constant of the base \((K_b)\) constant, the concentration of ammonium hydroxide (NH4OH) molecules is increased, so that addition of ammonium chloride (NH4Cl) to the reacting solution suppresses the ionization of the ammonium hydroxide (NH4OH) thereby, leading to decrease in the pH of the solution [14].

3.0. Applications of Common ion Effect in Chemistry

The common ion effect is a very useful phenomenon whose application in the laboratory is greatly established in salt analysis. Processes involving the phenomenon (figure 1.) are as discussed in the section below.

Figure 1. A schematic diagram of areas of application of the principle of common ion effect in chemistry.

The principle of common-ion effect applies in many chemical processes including those involved in buffering solutions, purification of salts, salting out of soap, precipitation of salts, manufacture of baking soda and water treatment (This study).
3.1. Purification of common salts

The principle of the effect of a common ion is well seen in reactions that involve purification of salts as the addition of common ion to a saturated solution of a salt causes the precipitation of the salt [15]. This suggests that the common salt, sodium chloride (NaCl) can thus be purified from its impurities; sodium tetraoxosulphate VI acid (Na$_2$SO$_4$) and magnesium tetraoxosulphate VI acid (Mg$_2$SO$_4$) upon application of this principle.

Pure NaCl can be precipitated by passing hydrogen chloride (HCl) gas in the saturated solution of impure NaCl [15].

\[
\text{NaCl}(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq).
\]

The passage of pure hydrogen chloride gas (HCl) through the above solution, itself being a strong electrolyte, leads to a complete dissociation of same and results in an increase in the concentration of chloride ions (Cl$^-$) (common ions) in the preparation. This causes a shift in equilibrium towards the left in accordance with Le Chatelier’s principle. With the prevailing condition, dissociation of NaCl is suppressed and pure NaCl is precipitated as solid salt [15].

\[
\text{HCl} (aq) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq).
\]

Similarly, pure Barium can be precipitated as barium tetraoxosulphate (vi) (BaSO$_4$) upon addition of tetraoxosulphate (VI) acid (H$_2$SO$_4$) to the solution [15].

\[
\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq).
\]

Upon addition to the above solution, H$_2$SO$_4$, being a strong acid, dissociates completely in the following way:

\[
\text{H}_2\text{SO}_4 (aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq).
\]

The addition of the tetraoxosulphate (vi) acid (H$_2$SO$_4$) and its subsequent dissociation in the solution results in increase in concentration/availability of common ions (SO$_4^{2-}$) sulphate ions, which in turn, shifts equilibrium to the left side of the reaction resulting in the precipitation of Barium as Barium tetraoxosulphate (vi) (BaSO$_4$) [15].

\[
\text{BaSO}_4(s) \downarrow \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq).
\]

3.2. Salting out of soap

In the preparation of soap by hydrolysis of oils with sodium hydroxide (NaOH) the occurrence of common ion effect is observed. The addition of a common ion to a saturated solution of a salt causes the precipitation of the salt [15]. Following this assertion, solid soaps are recovered from soap solution by addition of salt such as sodium chloride. Based on the principle described earlier, when ionic product exceeds the solubility product, precipitation takes place.

\[
\text{RCOONa}_{(aq)} \rightarrow \text{RCOO}^-_{(aq)} + \text{Na}^+_{(aq)}.
\]

Addition of a small amount of sodium chloride (NaCl) to the saturated soap solution causes the former to dissociate as follows:

\[
\text{NaCl}(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-_{(aq)}.
\]

Addition of Sodium chloride and its subsequent dissociation in solution results in increase in the concentration of sodium ions (Na$^+$) (common ion) in the preparation, which in turn, decreases the dissociation of soap so that the soap gets precipitated and can then be easily removed from the soap solution [15]. The soaps precipitate due to a combination of common-ion effect and increased ionic strength.

3.3. Qualitative salt analysis.

3.3.1. Precipitation of Sulphides of Group II.

A favourable condition for precipitation of any electrolyte to occur is that the concentration of its ions exceeds the solubility product ($K_{sp}$). This is obtained only when the concentration of any one ion is increased. Thus, by adding a common ion, the solubility product can be increased in such a degree causing precipitation [9]. In order to precipitate the Sulphides of the group II, hydrogen sulphide gas (H$_2$S) is passed through the original solution in presence of hydrogen chloride (HCl).

\[
\text{H}_2\text{S} \rightarrow 2\text{H}^+ + \text{S}^{2-}
\]

In the preceding reaction, HCl furnishes H$^+$ as common ions, which shift the above equilibrium to left according to Le-Chatelier’s principle. The addition of HCl to the solution suppresses the ionization of H$_2$S thereby lowering the concentration of sulphide ions (S$^{2-}$), in a manner just enough to exceed the solubility product of the group II Sulphides. In this way group, II cations such as Cu$^+$, Pb$^+$, Cd$^+$ can thus be precipitated [9].

3.3.2. Precipitation of Sulphides in Group III

Group III cations are precipitated as hydroxides by the ammonium hydroxide (NH$_4$OH) in the presence of ammonium chloride (NH$_4$Cl) [9]. In the above case, the common ion is NH$_4^+$, which suppresses the ionization of NH$_4$OH.

\[
\text{NH}_4\text{OH} \rightarrow \text{NH}_4^+ + \text{OH}^-
\]

Thus, with the addition of the common ion (NH$_4^+$), the equilibrium is shifted towards left and the concentration of
hydroxyl ions (OH⁻) decreases. Under these conditions, the solubility products of hydroxides of aluminum (Al), iron (Fe) and chromium (Cr) are only exceeded and as a result, they are precipitated. However, the hydroxides of the other cations such as zinc (Zn), nickel (Ni) and cobalt (Co) are not precipitated due to their higher solubility product [9].

3.3.3. Precipitation of Sulphides of Group IV

In qualitative analysis, group IV Sulphides having higher solubility product are precipitated by hydrogen sulphide (H₂S) in the presence of ammonium hydroxide (NH₄OH). The hydroxyl ion OH⁻ of NH₄OH combines with the hydrogen ion H⁺ of H₂S to form water H₂O:

\[ H^+ + OH^- \rightarrow H_2O \]

The removal of H⁺ from the product side shifts the equilibrium to the right [9].

\[ H_2S \rightarrow 2H^+ + S^{2-} \]

In this way, the concentration of the sulphide ion (S²⁻) increases in a rate which is enough to exceed the solubility product for the precipitation of sulphides, e.g. CoS, NiS, ZnS.

3.4. Manufacture of sodium bicarbonate: Solvay process

Common-ion effect is also observed in considering sodium bicarbonate, existing as a decahydrate compound (Na₂CO₃·10H₂O), which is manufactured by Solvay process in industrial scale, and have industrial and domestic uses [16]. The common ion effect is used in maintaining the buffer solution of (NH₃+NH₄Cl) when the brine is precipitated as sodium bicarbonate [17]. The Solvay process results in soda ash Sodium trioxocarbonate IV (Na₂CO₃) from brine (NaCl) and from limestone (CaCO₃) [18].

\[ 2NaCl + CaCO₃ \rightarrow Na₂CO₃ + CaCl₂ \]

The overall reaction is a complex one [19-20] but the principle is that once the saturated solution of sodium chloride (NaCl) is saturated with ammonia and carbon dioxide, the sodium bicarbonate will be precipitated from the solution. Sodium bicarbonate is generally soluble in water, but its solubility sharply decreases in a concentrated solution of NaCl, and thus causing the sodium bicarbonate to be precipitated [21].

\[ NaCl + CO₂ + NH₃ + H₂O \rightarrow NaHCO₃ + NH₄Cl \]

A more detailed procedure of the manufacturing process (figure 2.) has already been described [22] as shown in the diagram below.

![Figure 2. Outline for the manufacturing process of Sodium Carbonate via the Solvay process [22].](image-url)

The various stages of the process involve are shown in colours. The green towers marks Brine purification (Ammonia absorber which involves saturation of brine with ammonia), carbonation tower, calcination of sodium bicarbonate, and ammonia recovery tower; the blue bands represent filtration; while the red peaks represent application of heat.
3.5. Softening of hard water

Removal of dissolved calcium and magnesium salts that cause hardness in water can be achieved by adding chemicals that form insoluble precipitates such as calcium hydroxide (slaked lime) and sodium carbonate (soda ash) or by the use of ion exchange system [23-24]. Addition of the highly soluble sodium carbonate and/or calcium hydroxide salt to raw water causes the precipitation of the sparingly soluble calcium carbonate and/or magnesium hydroxide by common-ion effect [25]. Lime, though not a true coagulant, can react with the bicarbonate alkalinity to precipitate calcium carbonate. Whereas, magnesium hydroxide can form precipitate at high pH levels. Upon interaction, the lime and caustic soda can breakdown the bicarbonate ions (HCO$_3^-$) into water molecules and insoluble carbonate ions (CO$_3^{2-}$) in the following ways.

\[
\text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}.
\]

\[
2\text{NaOH} + \text{Ca(HCO}_3\text{)}_2 + \text{Ca}^{2+} \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O} + 2\text{Na}^+.
\]

In a basic solution, NaHCO$_3$ is less water-soluble than sodium chloride. The ammonia (NH$_3$) buffers the solution at a high pH (basic); without the ammonia, a hydrochloric acid byproduct would render the solution acidic, and arrest the precipitation [21].

However, the partial solubility of because calcium carbonate and magnesium hydroxide in water limits the limits potential of cold lime softening. Hot lime softening portends to an alternative but is not applicable to potable water [25]. Removal of precipitates after the softening is done by allowing water to sediment before filtration.

The common ion effect has been found also be useful in the treatment of wine waste-waters, which helps to obtain the organic compounds present in the waste from the wine making process, for example Tartaric acid, that can be used as additives in the food and pharmaceutical industries [26-27].

4. Authors’ Perspective

The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance has an effect on the solubility of the compounds. A regular occurrence when a new substance having a common ion is added to an already saturated salt solution is a reduced solubility of the original salt and a subsequent precipitation of some of the original salt out of the solution as solid crystals. Basically, the common-ion effect can be used to separate compounds or to remove impurities from mixtures. Scientists could take advantage of this property when purifying water and other substances. Having established the applications of the common-ion effect in chemistry, we note here however, that studies of occurrence of the phenomenon in processes involving areas like Biology, Geology, Forensics, Cosmetics and Environmental sciences have been scarcely reported. Knowledge of common ion effect is very important in physical chemistry and analytical chemistry as it is frequently applied in qualitative analysis. In relation to the above, the idea of common-ion effect needs to be taken into consideration whenever analyses of reactions involving salt solutions are to be carried out.

5. Conclusion

In this review, we have described the principle of common-ion effect as an important phenomenon being one major factor that affects the solubility of ionic substances. The review establishes that the presence of common-ion on an equilibrium reaction system can affect solubility and initiate selective precipitation. At the moment, common-ion effect appears to be a regular occurrence in many chemical processes, including the extraction of salt form sea water, purification of salts, qualitative analysis, water treatment, soap manufacture, regulation of buffers and precipitation of useful ingredients for food and pharmaceutical applications. Better understanding of its principles is necessary for proper implementation and execution.

References


