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Behavior of some chloride, carbonate, phosphate, sulphate and borate additive salt–NaCl aqueous solution systems in the absence and presence of NaF

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ABSTRACT

The objective of this investigation focuses to the behavior of the contact of some seawater's constitutes in both untreated discharged waters that fall along the coastal zone, and seawater in absence and presence of high fluoride concentrations. Fluoride is classified as one of the hazard contaminants for marine ecosystem when its concentration exceeds the range of 1.2–1.5 mg/l for unpolluted seawaters. The pH change in twelve aqueous systems containing additive salts ($CaCl_2$, $MgCl_2$, KCl, NH_4Cl, $NaHCO_3$, Na_3PO_4, Na_2SO_4 and $B(OH)_3$; known by their interfering properties among fluoride ion in seawater) and sodium chloride was followed in absence and in presence of sodium fluoride. Different concentrations of additive salts (similar and higher to seawater composition) were used to represent the behavior of these constituents in seawater and in the discharged water when they contact with the high fluoride concentration. $Ca(OH)^+$, CaF^+, $Mg(OH)^+$, $Mg(OH)_2$, MgF^+, $K(H_2O)_4^+$, $NH_4(H_2O)_n^+$, NH_4F, Na_2CO_3, HCO_3^-, $NaSO_4^-$, $B(OH)_4^-$ and BF_4^- species were formed in the studied systems. The concentration of the formed species and their equilibrium constants and solubility products were calculated. The results refer to the primary possible prediction of the formed fluoride species with the constituents of seawater along the coastal zone that is subjected to different huge discharged fluoride compound. Recalling that, some of these compounds are documented by their adverse effects on marine ecosystem.

Keywords: Twelve additive salt–NaCl aqueous solution systems; Sodium fluoride; pH change; formed species; equilibrium constant ;solubility product

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1. Introduction

Fluoride is one of the major constituents of seawater with a concentration of 1.3 ppm [1–3]. Its reported speciation in seawater is of 46% MgF^+, 2% CaF^+ and F^- 51% [1–3]. The recorded unpolluted water range for fluoride is of 0.5–1.5 mg/l [3]. Egyptian coastal seawater has become as a large scale collector for wastewater from different sources. It receives huge amounts of discharged wastes from El-Tapia pumping station, the main sewage out falls, Edku, Burullus and Manzalah lakes, El-Umum drain and some minor sewage outfalls located on it [4,5]. According to the industrial development and the consumption of more process water and chemicals, fluoride variability problem along the coastal line has become as a reasonable result. As any pollutant, fluoride enters the marine environment as byproducts of industrial and agricultural wastes beside drainage and domestic waters. Hydrofluosilicic acid, sodium silicofluoride and sodium fluoride are the byproducts of phosphoric acid

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manufacture [6]. Fluoride is also produced during the manufacturing of toothpaste, where stannous fluoride and sodium monofluorophosphate are used [6]. Fluoride pollutions from aluminum smelter are of a gaseous HF and in particulate form as Al_2O_3 with adsorbed HF, $NaAlF_4$, $Na_5Al_3F_{14}$ (chiolite), Na_3AlF_6 (cryolite), AlF_3, NaF, KF and CaF_2 [6]. Additionally, the byproduct of textile, fertilizers, rayon paper and pulp, aluminum smelters, chemicals and pharmaceutical industries wastes, contain fluoride compounds [3,6–11]. Additionally, semiconductor and display panel produce byproducts containing high fluoride concentrations and other pollutants such as ammonia, nitrate, and phosphate [3].

Many produced fluoride compounds are widely used in several industrial purposes. Ammonium silicofluoride and sodium fluoride are used in drinking water fluoridation [2]. Also, potassium fluoroaluminate ($KAlF_4$) is used in welding, soldering agents and abrasive process [3]. Hydrofluoric acid has the ability to dissolve glass [12]. Hexaflourosilicic acid (H_2SiF_6) and sodium heaxfluorosilicate (Na_2SiF_6) are commonly used as additives. Fluoride sources such as sodium fluoride and tetra-n-butylammonium fluoride (TBAF) are used in synthetic organic chemistry. Beryllium fluoride and aluminum fluoride are applied as phosphatase inhibitors. Sulfur hexafluoride is involved in electrical transformers [12]. Uranium hexafluoride is used in preparation of nuclear reactor fuel and atomic bombs. Fluoropolymers such as polytetrafluoroethylene, Teflon, are used as chemically inert and biocompatible materials for a variety of applications, including implants surgeries (coronary bypass grafts, and a replacement for soft tissue in cosmetic and reconstructive surgeries), non-stick surfaces (cookware and bake ware) and the fluoropolymer fabric Gore-Tex (breathable garments for outdoor) [12]. Additionally, fluoride is also a part of large variety of drugs including: antipsychotics such as fluphenazine, HIV protease inhibitors such as tipranavir, antibiotics such as ofloxacin and trovafloxacin, and anesthetics such as halothane. These compounds are incorporated in the drug structures to reduce drug metabolism, as the strong C–F bond resists deactivation in the liver by cytochrome P450 oxidases [12]. PVDF (polyvinylidene fluoride) is a constructive material in membrane synthesis [13]. Fluoride is widely used for preparing of cryolite, fluxes, enamels, glasses, and other minerals. Ammonium hexafluorosilicate is widely involved in chemical, woodworking, food, and other industries [14]. The recent use of sulfuryl fluoride, a structural fumigant in wood preservation is increased [15]. The species such as AlF_3 and AlF_4^- are able to simulate PO_4^{3-} group in many biochemical reactions [16].

The annually amount of fluoride is discharged into seawater through both land and drainage waters [17]. The uptake of fluoride from seawater by marine sedimentation was reported [17]. Carbonate and phosphate sedimentation remove from 10 to 20% fluoride ions discharged into seawater. Fluoride can incorporate calcium carbonate (aragonite or calcite) in seawater to form fluorapatite compounds [18]. The coprecipitation of fluoride ions with calcium carbonate is controlled by the crystal form of calcium carbonate and the presence of certain cations such as magnesium, copper and zinc ions beside some organic compounds (citrate, malate, lactate, etc.) in seawater as well as carbonates precipitation [18]. Fluoride can form different forms including, NH_4F, MgF_2, CaF_2 and fluorapatite ($Ca_5(PO_4)_3F$) in marine environment [3,14]. Aluminofluoride complexes (AlF_x) can be formed spontaneously in aqueous solutions containing fluoride and traces of aluminum ions [16]. The remaining discharged fluoride ions are removed as sea spray emitted from the surface to the air and returns back to seawater again through river and atmospheric precipitation [17].

NOS (National Organic Standards) allowed a rule in March 2000 for the use of pesticides that containing fluoride as their safety to environment [19]. But, the US Department of Agriculture's (USDA) revised this rule and finalized it in December 2000. It stated that fluoride is a persistent and non-degradable poison. It accumulates in soil, plants, wildlife, and humans. Additionally, the Agency for Toxic Substances and Disease Registry (ATSDR) pointed to the toxic effects of fluoride and its compounds on human being [19]. Fluoride damages the bone of the elderly, and interferes with the functioning of the brain, thyroid gland, pineal gland, kidney, and reproductive system [19].

Seafood is considered as a major source of fluoride. It accumulates in the hard tissues rather than the soft ones of marine organisms. Interestingly, the flesh of Egyptian marine fish contains permissible fluoride levels for food (100 mg/kg) and there is no risk from nutrition by fish [20,21].

The aim of this work is to study the behavior of systems containing additive salts (chloride, carbonate, phosphate, sulphate and borate; constituents of seawater), known by their interfering with fluoride ion and NaCl by following the pH change in absence and presence of NaF. The concentration, the equilibrium and solubility of the formed species in the systems are calculated.

2. Experimental

2.1. Apparatus

The used apparatus was formed of 10 ml mico-burette, 250 ml conical flask; Crison (Alella, Spain) 52-09 glass electrode and digital pH meter (model Extech 607, precision of 0.01 pH unit).

2.2. Prepared solutions

Sodium chloride (NaCl) stock solution of 1.197 M (the base solution for seawater of 35‰), selected additive solutions ($CaCl_2$, $MgCl_2$, KCl, NH_4Cl, $NaHCO_3$, Na_3PO_4,

Table 1
NaCl concentrations and initial concentrations of additives solutions for the different investigated systems

System number	Concentration of NaCl (M)	Additive	Concentration of the additive (M)
1	5.983	$CaCl_2$	0.876
2	5.983	$CaCl_2$	3.581
3	2.992	$MgCl_2$	1.026
4	2.992	$MgCl_2$	4.274
5	2.992	KCl	1.000
6	2.992	KCl	4.000
7	2.992	NH_4Cl	1.000
8	2.992	NH_4Cl	4.000
9	2.992	$NaHCO_3$	1.000
10	2.992	Na_3PO_4	1.000
11	2.992	Na_2SO_4	1.000
12	2.992	$B(OH)_3$	1.000

Na_2SO_4 and $B(OH)_3$) with different initial concentrations (Table 1) and sodium fluoride (NaF), input solution of 5.286×10^{-3} M were prepared. All the used solutions were of analytical grade (Merck and Sigma).

2.3. Different composed systems

Each system (1–12 systems) was composed of a mixture of a certain concentration of selected additive solution (dropping from the micro-burette) and a definite concentration of NaCl solutions (59.829, 5.983 and 2.992 M) placed in the conical flask (Table 1).

2.4. Experimental procedure

The used pH meter was calibrated by 4, 7 and 9 aqueous standard buffers from Crison at 19°C. The procedure was performed in two steps, first step was the formation of the different systems and second one represented the addition of sodium fluoride solution to each system.

For each system, the pH change belongs to the gradual addition of an additive solution from the mico-burette (milliliter, mL) onto the definite concentrations of NaCl (59.829, 5.983 and 2.992 M, Table 1) was recorded. Sodium fluoride solution (5.286×10^{-3} M) was added gradually to each separate system after the constancy of pH. Again, the pH change was recorded after adding the fluoride solution until its constancy. The conical flask was gently shaked to mix each system before and after sodium fluoride solution addition. The added volume (for each additive and fluoride solutions, milliliter, mL) onto the NaCl stock solution against the pH change in absence and presence of sodium fluoride for each system was plotted. Accordingly, these plots simply showed the step or different steps belong to the formed species in the absence and presence of NaF solution in the different systems.

2.5. The determination of the formed species and their concentrations

The obtained plot for each system showed the step or/and steps belong to the formed species at certain pH values. The hydrogen ion concentration, [H^+] was determined using the following well known equation [22,23]:

$$pH = -\log_{10}\left(\left[H^+\right]\cdot a_{H^+}\right) \tag{1}$$

where [H^+] and a_{H^+} are the hydrogen ion concentration and activity coefficient value, respectively. In solutions where the ionic strength is very low, the activity coefficient is 1.00 making the activity of hydrogen ion equals to its concentration. As the ionic strength of a solution increases, the activity coefficient decreases. This has the effect of lowering the activity of hydrogen ion which is seen as an increase in pH. From literature [24–29], the formed chemical formulas of species with their chemical transformations in seawater were known. These chemical formulas were applied in the calculations of the species' concentrations in the different systems using the volumes of additive solutions and the pH change in absence and presence of the mixed NaF solution. However, from the volume, the weight of the additive solution or input one can be deduced and accordingly the number of molecules involved in the formed species. If the reaction equation is known, it is possible to calculate the masses of reactants and products by using known atomic and molecular weights. In chemical terms, the amount of a substance is expressed in moles. For example, the equilibrium between calcium carbonate and its dissolved calcium and carbonate ions (atoms or molecules that have lost or gained electrons, with the number lost or gained shown as a positive or negative superscript) is represented as:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \tag{2}$$

One mole of a substance is the amount that contains as many elementary entities as there are atoms in 12 g of carbon. This number is termed Avogadro's constant, and its value is equal to 6.022×10^{23}. In the chemical equation given above for the equilibrium of $CaCO_3$ and its dissolved chemical species, one mole of $CaCO_3$ will dissolve in water to make one mole of Ca^{2+} and one mole of CO_3^{2-}. In terms of mass, 100 g of $CaCO_3$ will react to give 40 g of Ca^{2+} and 60 g of CO_3^{2-}. If only 10 g of $CaCO_3$ dissolves, then the same proportions of Ca^{2+} and CO_3^{2-} will be present at the equilibrium: 4 and 6 g, respectively. Accordingly, in the present work, from the number of H^+ the number of the different present and formed species will be calculated and then the concentration for these species expressed by moles is deduced.

2.6. The equilibrium constant and solubility product calculations for the formed species

These parameters were calculated from the concentration of these species for each system in the absence and presence of sodium fluoride solution using the chemical equations from the literature [24–29]. Concerning that, the step/or steps of the formed species in each plot are the shoulder/or shoulders at which pH remains constant.

3. Results and discussion

The equilibrium constant and solubility product for the formed species in each system are calculated and the values are discussed.

3.1. Systems 1 and 2

The gradual addition of 0.876 M and 3.581 M calcium chloride ($CaCl_2$) solution to 5.983 M NaCl solution in systems 1 and 2, respectively, show a pH increase in the 1st step. This pH increase deals with the formation of $Ca(OH)^+$ ion pair followed by the precipitation of $Ca(OH)_2$ in the 2nd step beside the existence of Ca^{2+} (Table 2). However, 91% of Ca^{2+} are in the ionic form in seawater [24]. For pH values of 7.00 and 8.25 (1st step) and $CaCl_2$ and NaCl stoichiometries of 1 : 2 and 1 : 1, respectively, Ca(OH)+ ion pair is formed with concentrations of 1.000×10^{-7} M and 5.623×10^{-9} M and K values of 1.070×10^{-6} and 1.256×10^{-9} in systems 1 and 2, respectively (Table 2). It was reported that $Ca(OH)^+$ formation is of minor existence in seawater and can be expressed as follows [24]:

$$Ca^{2+} + OH^- \rightleftharpoons Ca(OH)^+$$
$$K = \left[Ca(OH)^+\right]/\left[Ca^{2+}\right]\left[OH^-\right] \tag{3}$$

The decrease in equilibrium constants for $Ca(OH)^+$ from system 1 to 2 reflects the minimum existence for $Ca(OH)^+$ ion pair in system 2, i.e. high remaining concentration of $CaCl_2$ (3.581 M). However, the concentration of Ca^{2+} in system 2 solution is greater than that in system 1. Accordingly, the addition of 0.876 M and 3.581 M $CaCl_2$ solutions to 5.983 M NaCl solution in both systems 1 and 2 leads to the precipitation of $Ca(OH)_2$ with concentrations of 3.981×10^{-8} M and 5.623×10^{-10} M and K_{sp} values of 5.189×10^{-8} and 5.800×10^{-12}, respectively (Table 2). For system 1, very small concentration is evaluated for $Ca(OH)_2$ with higher K_{sp} value than that for system 2. Whereas, it is possible to find $Ca(OH)^+$ ion pair species due to its considerable reported thermodynamic association constant (20.0) [30]. Meanwhile, the lower performed temperature value of 19°C for the present investigation possibly interprets the higher pK values for $Ca(OH)_2$ species (7.28 and 11.24) than that previously recorded (pK = 5.19; 25°C) [25].

The gradual addition of NaF solution to system 1 gives an insignificant pH change beside the common abundance of Na^+ and F^-. This insignificant pH change may attribute to the strong coulumbic interactions among the ions. For system 2, the pH value decreases from 7.60 to 6.70 and from 6.70 to 6.60. However, the 1st step of pH 7.30 and 0.015 M NaF concentration reflects the formation of HF (formation constant of HF was of 2.6 [31]), Table 3. Additionally, the formed $Ca(OH)^+$ species dissociates and the releasing Ca^{2+} combines with F^- forming the possible CaF_2 precipitate with a solubility product of 3.980×10^{-14}. However, the reported logarithmic solubility product (log K_{sp}) for CaF_2 (fluorite) was ranged from –10.40 to 10.51 for NaCl solutions of concentrations similar to seawater and infinite dilution, respectively [30–33]. For the present study, the higher calculated log K_{sp} value of CaF_2 than those recorded previously may refer to the lower

Table 2
Concentrations, equilibrium constants and solubility products of the formed species at different pH values in each system after the additives solutions addition

System number	pH	Stoichiometry (additive: NaCl)	Species	Concentration of species (M)	K and K_{sp}	pK
1	7.00	1:2	Ca^{2+}, $Ca(OH)^+$	1.000×10^{-7}	1.070×10^{-6}	5.97
	7.40	1:7	Ca^{2+}, $Ca(OH)_2$	3.981×10^{-8}	5.189×10^{-8}	7.28
2	8.25	1:1	Ca^{2+}, $Ca(OH)^+$	5.623×10^{-9}	1.256×10^{-9}	8.9
	9.25	2:1	Ca^{2+}, $Ca(OH)_2$	5.623×10^{-10}	5.800×10^{-12}	11.24
3	6.10	1:12	Mg^{2+}, $Mg(OH)^+$	7.940×10^{-7}	9.575×10^{-12}	11.02
	5.95	1:5	$Mg(OH)_2$	11.220×10^{-7}		
4	5.75	6:1	Mg^{2+}, $Mg(OH)^+$	19.950×10^{-7}	3.319×10^{-12}	11.48
	5.35	16:1	$Mg(OH)_2$	44.660×10^{-7}		
9	8.70	1:30	Na_2CO_3, HCO_3^-, H_3O^+, $NaCO_3^-$	2.000×10^{-3}	1.990×10^{-15}	14.7
11	5.40	1:1	$NaSO_4^-$		0.543×10^{-12}	12.27
12	4.55	1:15	$B(OH)_3$, $B(OH)_4^-$	0.200	3.980×10^{-9}	8.4

Table 3
Concentrations, equilibrium constants and solubility products of the formed species and the mixed NaF solution concentrations in each system

System number	Concentration of NaF (M)	pH	Species	Concentration of species (M)	K and K_{sp}	pK
1	0.015	7.30	HF CaF^+	5.0119×10^{-8}	2.4×10^{-4}	3.62
2	0.045	6.65	CaF_2	4.467×10^{-8}	3.980×10^{-14}	13.40
			HF	2.239×10^{-7}	2.400×10^{-4}	3.62
4	0.002	6.10	MgF^+, Mg^{2+}	7.940×10^{-7}	6.396×10^{-4}	3.19
9	2.640×10^{-3}	8.79	NaOH,			
	7.929×10^{-3}	8.88	$NaHCO_3$	1.333×10^{-9}	1.066×10^{-9}	8.97
	1.586×10^{-3}	8.95	H^+, CO_3^{2-}, Na_2CO_3			
10	3.304×10^{-4}	11.35	HPO_4^{2-}	2.239×10^{-3}	1.253×10^{-6}	5.90
	2.661×10^{-3}	11.43	$H_2PO_4^-$	2.661×10^{-3}	2.140×10^{-2}	1.67
12	1.730×10^{-4}	5.60	BF_4^-	3.980×10^{-9}		

temperature (19°C) and the higher salts concentrations for NaF and NaCl in system 2. Also, the acidic pH value for systems 1 and 2 reveals to the formation of CaF_2 precipitate (fluorite) which can precipitate in a pH range of 5.50–7.00 [25]. The relative similar concentrations of both $Ca(OH)_2$ and CaF_2 species reflect the formation of HF which leads subsequently to the dissociation of $Ca(OH)_2$ and the formation of CaF_2 precipitant at the slightly acidic solution (pH = 6.70). Whereas, the insignificant decrease obtained for pH from 6.70 to 6.60 for the 2nd step in system 1 is possibly coincident with the HF formation. Also, the reported –log K (3.19) of fluoride ion hydrolyses for the formation of HF species [25] is relatively similar to that calculated in the present study (3.62) (Table 3).

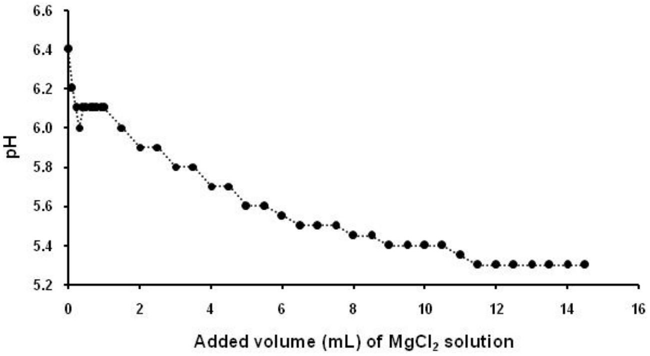

Fig. 1. The change in pH with the volume (mL) added of $MgCl_2$ (4.274 M) solution to system 4.

3.3. Systems 3 and 4

The addition of 1.026 M and 4.274 M magnesium chloride ($MgCl_2$) solution to 2.9915 M NaCl in the separate systems of [3] and [4] shows two definite steps for pH ranges of 6.10 and 5.95 and 6.10 and 5.35, respectively (Fig. 1). However, $Mg(OH)^+$ species can be formed at the 1st step with concentrations of 7.940×10^{-7} M and 19.950×10^{-7} M at pH values of 6.10 and 5.75 in systems 3 and 4, respectively. Additionally, the formation of the predominant species of Mg^{2+} at $MgCl_2$: NaCl stoichiometries of 1:12 and 6:1 for systems [3] and [4], respectively is detected (Table 2). For the 2nd step at pH of 5.35 in system [4] and $MgCl_2$: NaCl stoichiometry of 16:1, the solution of this system seems to be turbid due to the formation of $Mg(OH)_2$ precipitate. Accordingly, the low turbidity obtained in system 3 deals with the very low concentration of the formed $Mg(OH)_2$ precipitate of 11.220×10^{-7} M (Table 2). Additionally, the 2nd step of these systems contains the common ionic species of Mg^{2+}; however, 87% of magnesium in seawater exists in the free ionic form [24]. Meanwhile, Mg^{2+} can hydrolyse in seawater forming $Mg(OH)^+$ and $Mg(OH)_2$ species as follows [24]:

$$\begin{aligned} &Mg^{2+} + H_2O \rightleftharpoons Mg(OH)^+ + H^+ \\ &K = \left[Mg(OH)^+\right]\left[H^+\right]/\left[Mg^{2+}\right] \end{aligned} \tag{4}$$

System 3 shows a constant pH of 6.00 during the successive addition of 5.286×10^{-3} M NaF solution. The constancy in pH value for system 3 can be related to the insignificant coulombic interaction that exists between the ions in the low $MgCl_2$ concentration solution. In contrast, for system 4, a gradual increase in pH value from 5.30 to 6.10 is observed during the addition of NaF solution (Fig. 2). Also, the turbidity disappearance in this system in pH value of ≈6.10 indicates the formation of MgF^+ ion pair with concentration of 7.940×10^{-7} M and solubility constant (K) of 6.396×10^{-4} in the presence of Mg^{2+} free ions

(Table 3). The illustrated logarithmic value of both solubility constant and solubility product for MgF^+ ion pair and MgF_2 in seawater was of 1.30 and –6.70, respectively [34]. Thus, the higher calculated logarithmic *K* value (3.19) for MgF^+ of system 4 than that reported (1.30) may relates to its higher concentration in $MgCl_2$ solution (Mg:Cl stoichiometry of 16:1) and accordingly the higher coulombic interaction among these ions. However, the reported Mg:Cl stoichiometry for seawater is of 1 : 2 [24].

3.4. Systems 5 and 6

Mixing of 1.00 M or 4.00 M KCl solution with 2.992 M NaCl shows no change in pH in system 5 and gives a decrease in pH from 6.40 to 6.10 in system 6 (Fig. 3). Thus, the unchanged pH recorded during the gradual addition of 1 M KCl into NaCl in system 5 explains the electrostriction for the solvent in the diluted solution. Meanwhile, for system 6 (Fig. 3), the decrease in pH may refer to dissociation of KCl molecule. Whereas, the previous results illustrated that 99% of K in seawater are free ions existing in $K(H_2O)_4^+$ form [24]. Additionally, KCl is a strong electrolyte that is known by its complete dissociation in aqueous solution as other strong electrolytic solutions [24].

Gradual addition of 5.286×10^{-3} M NaF solution to system 6 (Fig. 4) gives insignificant pH changes of 6.20–6.00 and 6.60–6.00, respectively. The small pH variation probably combines with the high electronegativety of fluoride. However, tiny positive charges are formed at hydrogen atom of O–H bond causing a minimum decrease in pH value for high concentrated KCl solution in system 6. Thus, the insignificant change for pH value in system [6] can relate to the high columbic interaction among the existing ions.

3.5. Systems 7 and 8

The addition of 1.00 M and 4.00 M NH_4Cl solutions to 2.992 M NaCl gives a significant pH decrease from 6.20 to 5.80 and from 6.40 to 4.90 in systems 7 and 8, respectively (Fig. 5). This change in pH in both systems 7 and 8 may be accompanied by the hydration of NH_4Cl solutions. It was recorded that the hydration number and thermodynamic association constant for NH_4Cl were of 1.6 and 1.23, respectively [25]. Accordingly, NH_4Cl prefers to exist in the ionic forms in its solutions.

The successive mixing for 5.286×10^{-3} M NaF solution in systems 7 and 8 shows no pH change in system 7 and an insignificant pH increase from 4.90 to 5.00 (Fig. 6). For system 8, one step is detected concerning the formation of NH_4F beside NaOH species with negligible content which is not responsible for the pH increase. Accordingly, the pH change is accompanied with the existing NH_4Cl and NaF species. For system 7, small coulombic interaction among ions and electrostriction of solvent molecules may explain the absence of pH change. Meanwhile, system 8 of higher NH_4Cl concentration (4.00 M) shows the pH change due to the high coulombic interaction.

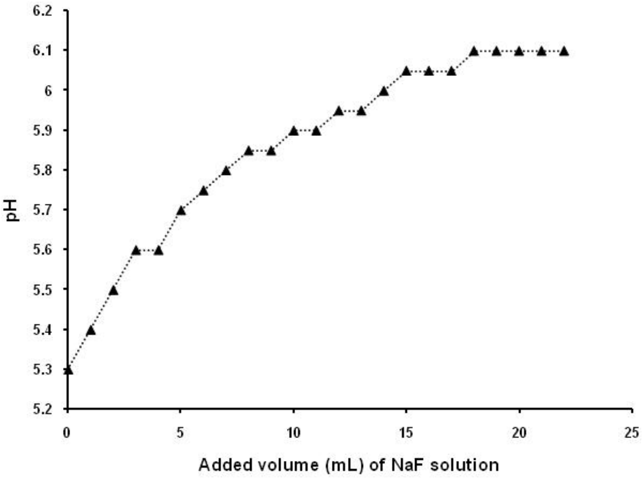

Fig. 2. The change in pH with the volume (mL) of NaF (5.286×10^{-3} M) solution added to system 4.

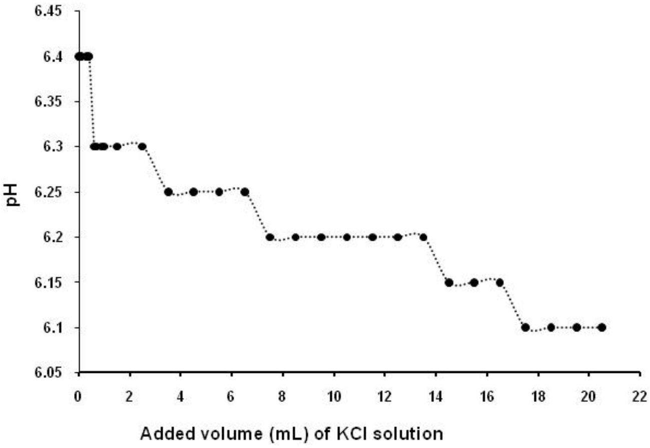

Fig. 3. The change in pH with the volume (mL) added of KCl (4.00 M) solution to system 6.

3.6. System 9

The gradual addition of 1.00 M $NaHCO_3$ to 2.992 M NaCl, system 9 shows a significant pH increase from 6.80 to 8.70. One step is observed at $NaHCO_3$: NaCl stoichiometry of 1:30 and possible formation of Na_2CO_3, HCO_3^-, H_3O^+ and $NaCO_3^-$ ion pair as well as $NaHCO_3$ species (2.000×10^{-3} M) (Table 2). Interestingly, the calculated $NaHCO_3$ concentration is relatively equal to that reported for seawater [35]. Also, the present result refers to the predominate existence of HCO_3^- species in this solution. Accordingly, this result goes in harmony with the previous work concerning the presence of HCO_3^- as a free ion

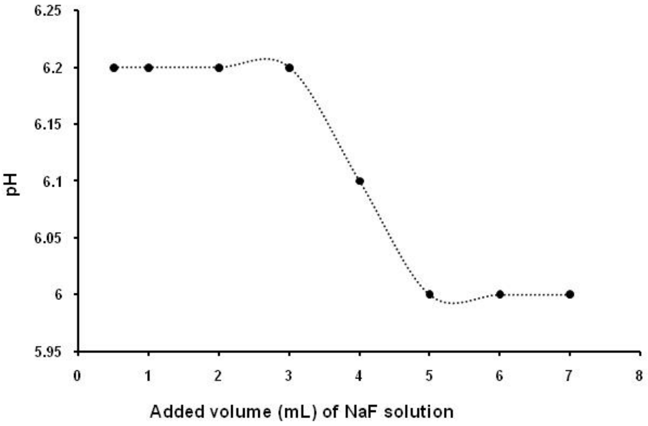

Fig. 4. The change in pH with the volume (mL) of NaF (5.2857×10^{-3} M) solution added to system 6.

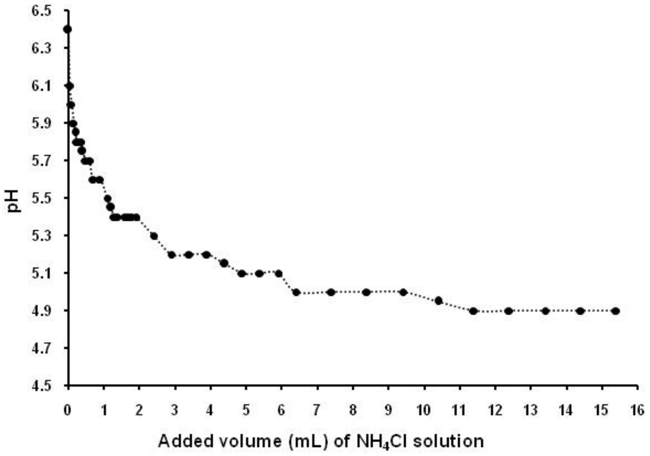

Fig. 5. The change in pH with the volume (mL) added of NH_4Cl (4.00 M) solution to system 8.

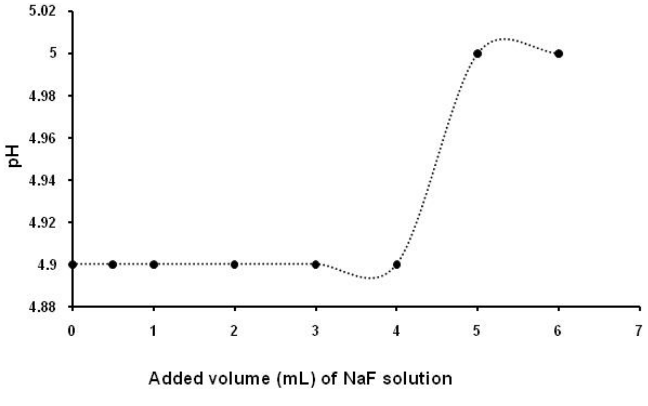

Fig. 6. The change in pH with the volume (mL) of NaF (5.2857×10^{-3} M) solution added to system 8.

in seawater by 69.0% [24]. Moreover, the recorded association constants for $NaHCO_3$ and $NaCO_3^-$ were of 0.46 and 2.0, respectively [25]. Meanwhile, the illustrated stability constant for $NaCO_3^-$ was of 4.16 [24]. On the other hand, the calculated equilibrium constant for HCO_3^- for the present work (1.99×10^{-15} at 19°C) is smaller than that recorded for aqueous solution (4.7×10^{-11} at 25°C) [26]. Thus, the difference between the deduced and the reported equilibrium constants may relate to the temperature value, concentration of solution, interaction between ions, etc.

The gradual addition of NaF (5.286×10^{-3} M) solution to system 9 induces the pH to increase from 8.7 to 9. Additionally, three steps are detected for pH values of 8.79, 8.88 and 8.95 and NaF concentrations of 2.640×10^{-3}, 7.929×10^{-3} and 1.586×10^{-3} M, respectively (Table 3). It is obvious that the 1st step relates to the ion pairs' formation of both NaOH and $NaHCO_3$, however, the documented association constants for NaOH and $NaHCO_3$ were 0.2 and 0.562, respectively [25]. The 2nd step deals with the dissociation of HCO_3^- species into H^+ and CO_3^{2-} and the probable formation of Na_2CO_3 ion pair. However, this steps coincident with the reported dissociation (18.6) and association (2.0) constants for HCO_3^- and Na_2CO_3 [25]. Additionally, the 3rd step refers to the formation of Na_2CO_3. The three steps can be expressed as follows:

$$NaHCO_3^- \rightarrow Na^+ + HCO_3^- \quad (5)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (6)$$

$$2Na^+ + CO_3^{2-} \rightarrow Na_2CO_3 \quad (3)$$

The dissociation constant for HCO_3^- species in the 2nd step in the presence of NaF is of 1.066×10^{-9} (Table 3). This dissociation constant is greater than that reported for aqueous solution (4.7×10^{-11}) [26]. Accordingly, the high electronegativity of NaF solution probably accompanied with this greater dissociation constant that refers to the faster dissociation for HCO_3^- species. The pH change for 1st, 2nd, and 3rd are 8.70–8.85, 8.85–8.90, and 8.90–9.00, respectively. So, the pH changes for the 1st and 3rd steps are greater than that for 2nd step. Thus, these pH changes confirm the reversibility of the 2nd step which deals with the dissociation of HCO_3^- into CO_3^{2-} and H^+ and the irreversibility of both 1st and 3rd steps (Table 3).

3.7. System 10

Insignificant pH change is obtained for the successive addition of 1.00 M Na_3PO_4 solution to system 10. This unchangeable pH system may reflect the presence of uninteracted free ions. The previous investigation gave concentration ratios of 10^{-1}, 10^{-2} and 10^{6} for $[PO_4^{3-}]/[HPO_4^{2-}]$, $[HPO_4^{2-}]/[H_2PO_4^-]$, and $[H_2PO_4^-]/[H_3PO_4]$, respectively at pH of 8. Thus, these concentration ratios showed the dominant existence of HPO_4^{2-} beside the presence of

PO_4^{3-}, $H_2PO_4^-$, and H_3PO_4 species [24]. Moreover, 99.6% and 44% of PO_4^{3-} and HPO_4^{2-}, respectively can complex with cations including Na^+ in seawater [25]. Additionally, 87%, 12% and 1% of inorganic phosphate exists in seawater as HPO_4^{2-}, PO_4^{3-} and $H_2PO_4^-$, respectively [25]. Accordingly, for system 10, HPO_4^{2-} can be considered as the predominant predictable species.

The gradual addition of NaF solution to system 10 shows an insignificant pH increase from 11.30 to 11.46. However, this pH increase refers to the formation of NaOH° ion pair and HPO_4^{2-} species as given:

$$H_2O + PO_4^{3-} \rightleftharpoons HPO_4^{2-} + OH^- \quad (8)$$

$$H_2O + HPO_4^{2-} \rightleftharpoons HPO_4^- + OH^- \quad (9)$$

Two steps are recorded at pH values of 11.30 and 11.40 and 11.40 and 11.46. So, the 1st step concerns the composition for HPO_4^{2-} species with concentration of 2.239×10^{-3} M and equilibrium constant of 1.253×10^{-6} (Table 3). This equilibrium constant is relatively similar to that previously recorded (0.41×10^{-6}) [25]. Whereas, the 2nd step relates to the formation of $H_2PO_4^-$ with a concentration of 2.661×10^{-3} M and equilibrium constant, K of 2.140×10^{-2}. The calculated K for $H_2PO_4^-$ in the present work is relatively similar to that previously estimated (2.28×10^{-2}) [25]. The reported results referred to the dependence of ion pair and complex species formation on the specific interactions among the constituents of the medium [25]. So, the slightly change in pH during the addition of NaF solution to system [10] may relate to its electronegativity and the coulombic interaction between the ions.

3.8. System 11

Gradual mixing of Na_2SO_4 solution to NaCl in system 11 shows a pH decrease from 6.70 to 5.40. For pH value of 5.40 and Na_2SO_4 : NaCl stoichiometry of 1:1, $NaSO4^-$ ion pair is formed in one step as follows:

$$SO_4^{2-} + Na^+ \rightleftharpoons NaSO_4^- \quad (10)$$

So, system 11 contains the formed ion pair of $NaSO_4^-$ beside the original predominant species of Na_2SO_4. The calculated equilibrium constant (K) for $NaSO_4^-$ (0.543×10^{-12}, Table 2) is relatively similar to that reported for the dissociation constant of SO_4^{2-} (1.0×10^{-12}) in aqueous solution [26]. The difference between the K values for the present study and previous investigation may relate to the experimental conditions (temperature, concentration, interaction between ions, etc.).

No pH change is observed during the continuous addition of NaF solution to system 11. This observation possibly refers to the concentration of ion pairs that is proportional to the volume occupied by free cations [25]. However, the probable ion pair formation is accompanied with the cation number as well as with the interaction coulombic energy among the ions that including the solution medium [25].

3.9. System 12

Successive addition of boric acid to NaCl, system 12, gives a pH decrease from 6.70 to 4.20. For a pH value of 4.55, $B(OH)_3$ concentration of 0.200 M and $B(OH)_3$: NaCl stoichiometry of 1:15, the $B(OH)_3$ species dissociates to $B(OH)_4^-$ and one liberating proton (Table 2). The following equation can describe this dissociation process:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad (11)$$

The calculated K value for $B(OH)_3$ of 3.980×10^{-9} is approximately equal to that recorded for artificial seawater (2.51×10^{-9}) [26]. Thus this equilibrium constant similarity indicates the existence of the common species, $B(OH)_3$ and $B(OH)_4^-$, in the system. However, the mainly dissolved boron forms in seawater are $B(OH)_3$ and $B(OH)_4^-$ [26,27].

The gradual mixing of NaF solution to system [12] gives a pH increase from 4.20 to 5.60 and fluoborate ion (BF_4^-) [7,36] is formed with a concentration of 3.980×10^{-9} M in one step (Table 3). Additionally, BF_4^- formation is accompanied with the hydroxyl group liberation at a pH value of 5.60 and sodium fluoride concentration of 1.730×10^{-4} M (Table 3). However, it was stated that fluoride may exists as a free ion (F^-) or soluble complexes such as SiF_6^{2-}, AlF^{2+}, AlF_2^+, AlF_3^0, AlF_4^-, BF_4^-, and HF [36]. The ionic form of fluoride predominates in a pH value above 6, whereas its various complexes predominate in lower pH values [36].

4. Conclusion

Naturally, fluoride combines with most elements to form inorganic and organic fluorides. In the environment, inorganic fluorides predominate over the organic ones. During last decades inorganic fluorides are subjected to an environmental concern although most of them are of natural origin. Recently, some inorganic fluorides are used in many purposes including, fluoridation, manufacture, pharmacy and human curing. So, the excessive use of fluorides in these various fields can leads to a marine pollution problem. The inshore marine environments always face huge amounts of drainage waters from different outlets. Fluorides, especially inorganic fluoride can interact with some marine components and create different forms that may accumulate, adsorb, or/and precipitate in marine environment.

To the point of view of fluoride and its interaction with some seawater constituents and its adverse effects on the marine ecosystem, this study was performed by using NaCl (35‰) solution as the base medium for seawater. Some solutions containing additive inorganic salts ($CaCl_2$, $MgCl_2$, KCl, NH_4Cl, $NaHCO_3$, Na_3PO_4, and $B(OH)_3$) that resemble some ionic seawater's constituents are gradually added to NaCl solution to form twelve systems. However, these systems contain chloride, carbonate, phosphate, sulphate and borate additive salts with concentrations similar and higher than that of seawater composition. Also, these systems are subjected to successive addition of 5.2857×10^{-3} M NaF solution to study the separate fluoride effects on some ionic components of both seawater and discharged waters. The study of pH change inside these systems in the presence and absence of fluoride ion is recorded. Actually, pH change refers to the formation of different species ($Ca(OH)^+$, CaF^+, $Mg(OH)^+$, $Mg(OH)_2$, MgF^+, $K(H_2O)_4^+$, $NH_4(H_2O)_n$, NH_4F, Na_2CO_3, HCO_3^-, HF, $NaSO_4^-$, $B(OH)_4^-$ and BF_4^-) inside these systems. By calculating the hydrogen ion concentration, the equilibrium constants and the solubility products of these formed species in different systems are determined. Interestingly, the present calculated values for the equilibrium constants and the solubility products are in harmony with the previous data. Accordingly, many precautions must be applied towards the permissible drainage water composition as well as defluoridation must be performed to the drainage waters inside the factories or/and before throwing into coastal seawaters to overcome the hazardous effect of fluoride on marine environment, and consequentially on mankind in the long time exposure.

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