

Understanding the role of ion interactions in soluble salt flotation

Orhan Ozdemir¹, Hao Du², Stoyan I. Karakashev^{1,a}, Anh V. Nguyen^{1,b}, M.S. Celik³ and Jan D. Miller^{4,b}

¹School of Chemical Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia.

²National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China, 100190.

³Department of Mineral Processing Engineering, Istanbul Technical University, Istanbul, 34469, Turkey.

⁴Department of Metallurgical Engineering, University of Utah, Salt Lake City, Utah 84112, USA.

Abstract

There is anecdotal evidence for the significant effects of salt ions on the flotation separation of minerals using process water of high salt content. Examples include flotation of soluble salt minerals such as potash, trona and borax in brine solutions. Although some of the effects are expected, some do not seem to be encompassed by classical theories of colloid science. Several experimental and modeling techniques for determining solution viscosity, surface tension, bubble-particle attachment time, contact angle, atomic force microscopy, sum-frequency vibrational spectroscopy and molecular dynamics simulation have been used to provide further information on air-solution and solid-solution interfacial phenomena, especially the interfacial water structure due to the presence of dissolved ions. These studies indicate that the ion specific effect is the most significant factor influencing flotation in brine solutions.

Key words: flotation, soluble minerals, saline/brine solutions, dissolved ions, ion specific effect.

^a Current address: Department of Physical Chemistry, Sofia University, 1 James Bourchier Avenue, Sofia 1126, Bulgaria

^b Corresponding authors: Emails Anh.Nguyen@eng.uq.edu.au and Jan.Miller@utah.edu

1. Introduction

Froth flotation is one of the most important separation methods whereby hydrophobic mineral particles are captured by air bubbles and removed from the slurry into a froth phase. Particulate separations by flotation are of considerable significance in many areas of technology ranging from water treatment and materials recycling, to the mining and construction materials industries. Since froth flotation involves physico chemical phenomena at the solid/water (S/W) and at the air/water (A/W) interfaces, surface chemistry principles play a significant role in the development of improved flotation technology.

Soluble salt minerals (potash, trona, borax, etc.) are essential raw materials for the production of many different commodities; fertilizers, magnesium metal, magnesium oxide, soda ash, baking soda and many boron chemicals. These soluble mineral resources can be processed using flotation technology and, in fact, the use of flotation technology is critical for the potash industry. Since the flotation process for soluble minerals must be carried out in saturated solutions due to the high solubility of these salt minerals, the interfacial water structure is influenced and this affects collector adsorption at salt surfaces.

Dissolved ions in solutions can inhibit or activate the floatability of minerals due to their effect on the properties of the solutions and interfaces involved. The ions present at relatively high concentrations can significantly impact the colloidal interactions between bubbles and particles during flotation. The most important example, perhaps, for the effect of the dissolved ions in flotation is the soluble salt flotation of minerals such as potash, trona and borax. Since these minerals are soluble in water, a saturated solution is used to prevent solubilization of the floated salt particles from the gangue particles. Therefore, it is important to understand how the dissolved ions behave in solutions and at the interfaces. For instance, the flotation of potash minerals has to be carried out in a saturated brine of about 5 M of halite (NaCl) and sylvite (KCl). The highly concentrated salt solutions influence the bulk and interfacial water structure such that adsorption of flotation chemicals (e.g., insoluble collectors of long chain amines) at the minerals surfaces and air bubbles (Burdukova et al., 2009; Cheng et al., 2008). At high salt concentration, electrostatic interactions cease and thus zeta potential is almost zero, and the solubility of collectors is limited.

Fundamental understanding for the flotation of soluble salts is limited when compared with other flotation systems, e.g., oxides, silicates, sulphides and semisoluble salt minerals. For instance, flotation experiments of soluble alkali halide salts with dodecylamine hydrochloride (DAH) and sodium dodecylsulphate (SDS) collectors have demonstrated that KCl can be floated with both cationic (DAH) and anionic (SDS) collectors. However, NaCl (halite) cannot be floated with either of the collectors (Hancer et al., 2001). The electrical double-layer theory fails to explain the floatability of NaCl and KCl crystals in these saturated solutions. It is shown in the next section that the structure of water induced by the salt ions determines the salt floatability.

Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is another soluble salt, which must be upgraded to about 35% B_2O_3 for the production of basic chemicals, such as boric acid. Boron minerals; colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$), and kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$), exhibit a spectrum of chemical compositions with cations ranging from monovalent to multivalent ions. The type and valence of the cation dictate the solubility of the minerals and in turn their electrokinetic behavior. Borates release a number of species upon dissolving in water such as $\text{B}_4\text{O}_7^{2-}$. The ions released from boron minerals have been shown to interact with collectors to form insoluble surface precipitates.

The primary source of sodium carbonate (soda ash) in the United States consists mainly of trona, sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), containing minor undesirable gangue materials. Since sodium carbonate (Na_2CO_3) and bicarbonate (NaHCO_3) are the main constituents of trona, most of the studies have focused on the flotation of carbonate and bicarbonate salts (Ozcan and Miller, 2002). Micro-flotation studies with carbonate salts (Na_2CO_3 and NaHCO_3) showed that contrary to the strong flotation of NaHCO_3 with both anionic and cationic collectors, Na_2CO_3 does not float at all (Ozcan and Miller, 2002).

In the past, the flotation chemistry of soluble salts has received relatively little attention perhaps due to experimental difficulties such as high ionic strength, high viscosity and high pH in the case of trona and borax minerals. More recently efforts have been made to explain the mechanism of collector adsorption in soluble salt flotation systems. A number of experimental and modeling techniques have been used to develop a better understanding of the effect of dissolved salts on the flotation of soluble salt minerals as exemplified above.

In this paper, we use the results obtained by different methods to review the role of ion interactions in the flotation of soluble salts. The available experimental results have provided a better understanding of the flotation behavior of many systems, including potash, trona, and borax. Possible mechanisms and practical implications will be discussed to highlight the significance of ion interactions in brine solutions.

2. Flotation of typical soluble salts

The flotation process for soluble salt minerals such as potash, trona and borax is carried out in saturated solutions due to their high solubility. Such high salt concentration appears to have a significant effect on the interfacial water structure which influences the collector adsorption at the salt surface and also has an impact on the adsorption of collector at the surface of insoluble mineral components of the salt resource.

2.1 Potash flotation

Potash ores are a mixture of sylvite (KCl) and halite (NaCl) with water-insoluble minerals such as clay and carbonate minerals. Potash is widely used as fertilizer in the agriculture industry. Other uses for potash are glass manufacturing, soaps, plastics and pharmaceuticals (Perucca, 2003). Most of the potash ores in the world are concentrated by froth flotation.

Although there have been many studies on the flotation behavior of various soluble salts in their saturated solutions, the collector adsorption mechanism at the surface of soluble salts minerals is still not clearly explained (Rogers and Schulmann, 1957; Schubert, 1988; Miller and Yalamanchili, 1994; Laskowski, 1994; Hancer et al., 1997; Hancer and Miller, 1999; Hancer and Miller, 2000; Burdukova and Laskowski, 2009). There have been many models proposed to explain the flotation behavior of soluble salts in their saturated solutions such as ion exchange model (Fuerstenau and Fuerstenau, 1956), a heat of solution model (Rogers and Schulman, 1957), and a surface charge-ion pair model (Schubert, 1988). Recently, significant progress has been achieved in the areas of soluble salt flotation chemistry particularly by Miller and his co-workers (Hancer et al., 2001; Hancer and Miller, 2000; Miller et al., 1992; Yalamanchili et al., 1993). Subsequent research by Hancer showed that consideration of hydration phenomena at salt crystal surfaces provided a better explanation for the flotation of soluble salts even when the collector charge is the same as the salt (Hancer et al., 2001).

As seen in Figures 1 and 2, KCl can be floated with both cationic (dodecylamine hydrochloride) and anionic (sodium laurate) collectors. However, NaCl (halite) cannot be floated with either of the collectors (Miller et al., 1992). As mentioned above, in brines the double layer thickness is very small at salt surfaces, which make measurement of the surface

charge under these circumstances difficult. Nevertheless, surface charge measurements of salt minerals were first made using a nonequilibrium electrophoretic technique (Miller et al., 1992). This study showed that KCl has a negative surface charge, whereas NaCl has a positive surface charge and these results were used to explain the flotation of KCl from NaCl with 12C amines. According to this analysis, the positively charged amine collector colloid adsorbs on negatively charged KCl particles, while there was no adsorption of the cationic collector at the positively charged NaCl particles (Yalamanchili et al., 1993).

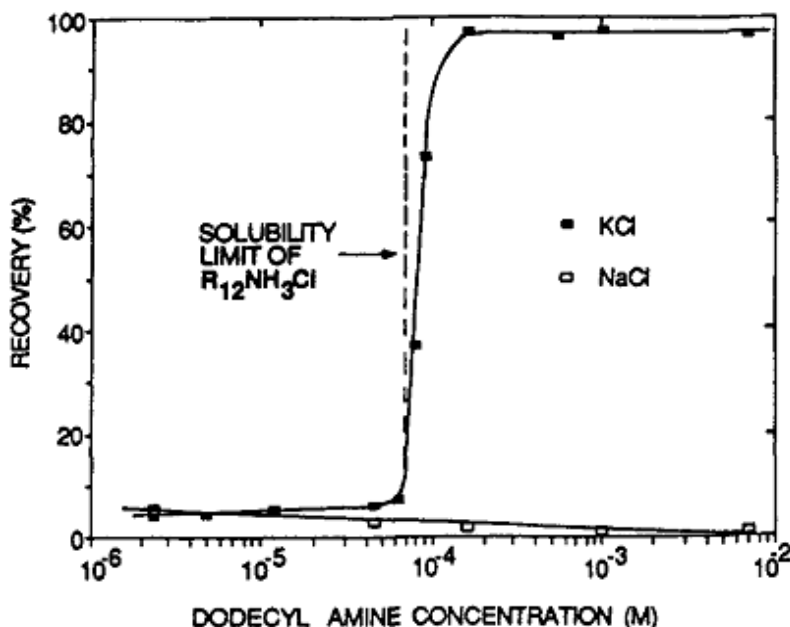


Figure 1. Flotation recovery of KCl and NaCl as a function of dodecylamine hydrochloride concentration (Miller et al., 1992).

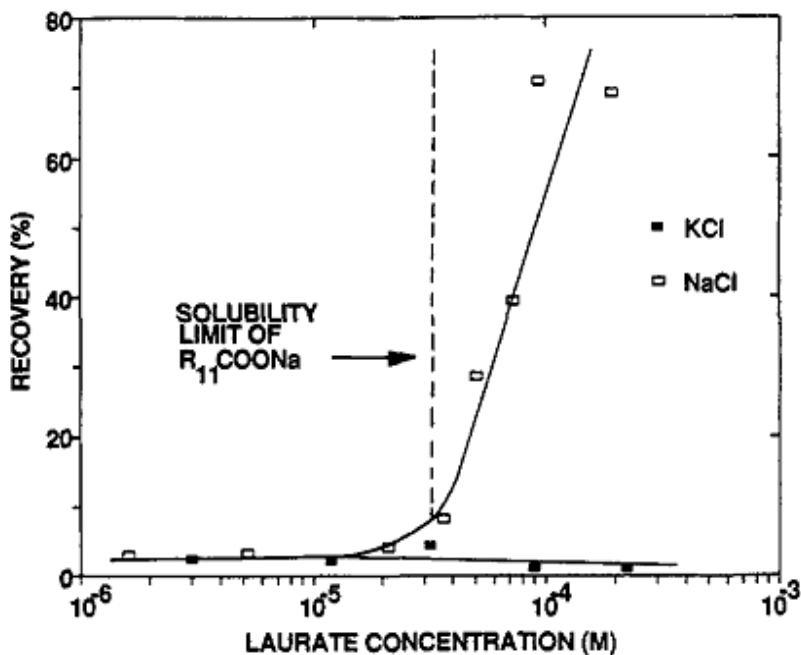


Figure 2. Flotation recovery of KCl and NaCl as a function of sodium laurate concentration (Miller et al., 1992).

Unfortunately this theory could not answer the question of why negatively charged KCl particles are also floated with 12C anionic collectors such as SDS. Subsequently research by Hancer showed that consideration of hydration phenomena at salt surfaces provides a better explanation for the flotation of alkali halide salts even when the collector charge is the same as the salt (Hancer et al., 2001). These studies and the analysis of surface hydration indicate that a salt may be either a water structure maker or a water structure breaker. If the salt serves as a structure maker for water, the water molecules will be strongly bonded at the salt surface and the adsorption of collector at the hydrated surface is prevented. As is well known, collectors generally must adsorb at the particle surface in order to create a hydrophobic surface state for flotation. Unlike the structure maker salts, the structure breaker salts have a tendency to destroy the structure of water at the salt surface; thus a collector may more easily reach the surface, create the hydrophobic surface state and thus allow for the flotation of such salts. Drawings which illustrate these cases are presented in Figures 3 and 4, respectively.

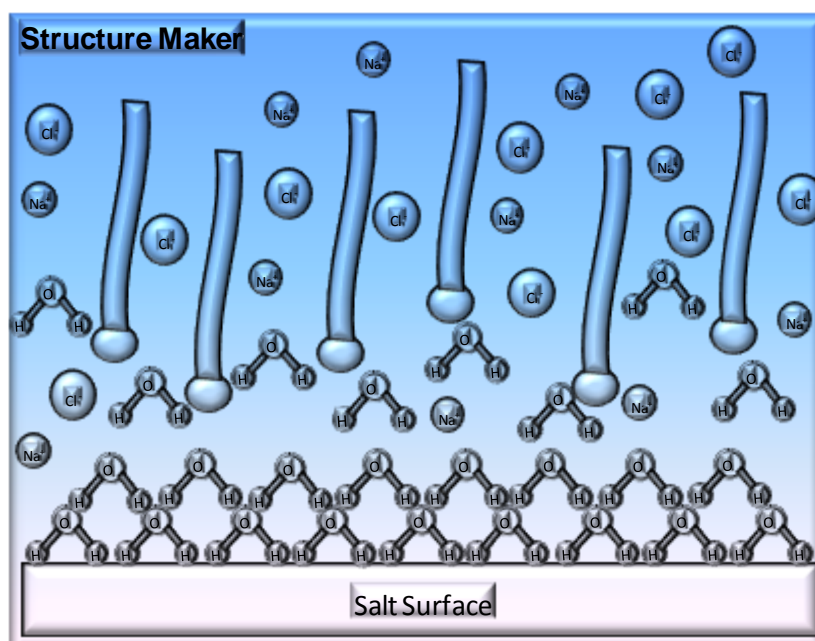


Figure 3. Collector Adsorption does not occur at the NaCl Surface for 12C amine and sulfate collectors (NaCl is a water structure maker) (Hancer et al., 2001).

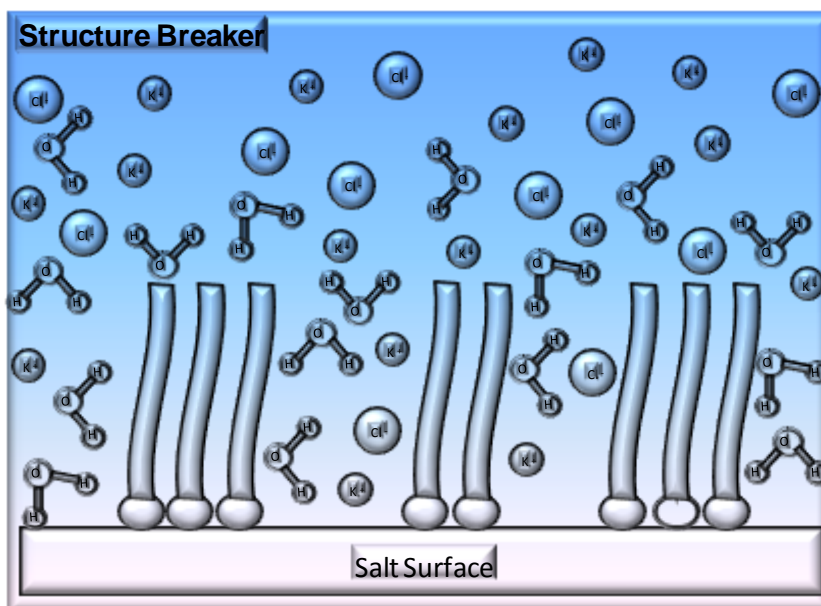


Figure 4. Collector adsorption does occur at the KCl surface for 12C amine and sulfate collectors (KCl is a water structure breaker) (Hancer et al., 2001).

The flotation response of the selected salts is presented in Table 1. As seen in Table 1, salts that can be floated with either the cationic (DAH) or anionic collectors (SDS) are the water structure breakers whereas salts that are classified as water structure makers stabilize the interfacial water structure at the salt-brine interface and the flotation of these salts with either collector is not possible.

Table 1. Correlation of floatability of alkali halide salts with water structure (Hancer 2001)

	F⁻	Cl⁻	Br⁻	I⁻
Li⁺	F	NF	NF	NF
Na⁺	NF	NF	NF	NF
K⁺	NF	F	F	F
Cs⁺	NF	F	F	F
Rb⁺	NF	F	F	F

NF: No flotation; F: flotation

A molecular dynamics simulation (MDS) study regarding water structures at LiCl, NaCl, KCl and RbCl salt surfaces in their saturated brine solutions is reported by Du and Miller (Du and Miller, 2007b; Du et al., 2007a). This study showed that water molecules are highly ordered at NaCl and LiCl surfaces with distinct orientations due to strong interaction between water molecules and small surface cations, Na⁺ and Li⁺. In contrast, water molecules oriented at KCl and RbCl surfaces randomly due to weak interaction between water molecules and large

surface cations such as K^+ and Rb^+ . This study also showed that the orientation of water molecules at the salt surfaces is not as simple as shown in the drawings.

2.2 Borax flotation

Borax ($Na_2B_4O_7 \cdot 10H_2O$), one of the most important boron minerals in the world, contains about 20% B_2O_3 when mined and must be upgraded to about 35% B_2O_3 for the production of basic chemicals, such as boric acid. The most commercially important boron minerals beside borax are colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$), and kernite ($Na_2B_4O_7 \cdot 4H_2O$). Apart from these minerals, a considerable amount of boron compounds is also produced from boron-rich lakes (Harben and Dickson, 1985).

Boron compounds are used in the manufacture of a variety of industrial products including advanced materials. World reserves of boron minerals are estimated at 1,241Mt B_2O_3 , sufficient to meet world demand at current levels for over 600 years (Roskill, 2010). The United States and Turkey are the world's two largest producers of boron compounds. Together, these two countries make up about 90% of the world's boron reserves (Harben, 1995).

Boron minerals show a spectrum of solubilities depending upon the cations in the lattice structure. While colemanite and ulexite are classified as semi-soluble minerals, borax and kernite are soluble minerals. Borax is normally concentrated from its saturated brine by scrubbing followed by classification. The friable nature of boron minerals, however, tends to produce a large amount of fines mostly below 0.2 mm which are usually discarded as waste. Recovery of these fines is possible only through particle separation processes such as flotation. In most boron ores, the major accompanying gangue minerals are montmorillonite type clays and carbonate minerals, and thus a common problem encountered in both classes of boron minerals is the presence of significant amounts of clay type minerals which adversely affect flotation recoveries in the form of slime coatings (Akin et al., 1997).

Despite the successful application of flotation technology in the potash industry, flotation has not yet been well developed for borax recovery. This may be attributed to inherent difficulties such as high ionic strengths, and particularly the presence of clay minerals, which act as persistent slimes. While Miller and his co-workers provided new insight into explaining the selective flotation of several soluble salt minerals from their saturated brines, Celik and his associates have identified some particular characteristics of the flotation behavior of boron minerals with cationic and anionic collectors (Celik et al., 1993; Celik and Bulut, 1996; Celik et al., 2002; Celik and Yasar, 1995). For example, as seen in Figure 5, both surfactants SDS and DAH float borax in the same manner at concentrations above 1×10^{-5} M. The lattice structure of borax is composed of Na^+ ions. This characteristics feature imparts high solubility to borax. Although the collectors used are usually less soluble in concentrated brine solutions, the floatability of boron minerals is enhanced in the presence of brine. The results indicate that there appears to be a direct correlation between the onset of flotation and that of hemimicelle formation. For borax it provided that the extent of CMC reduction in such saturated brines is known. It is well known that the CMC of sulfonate shifts by an order of magnitude in the presence of 0.1 M NaCl solutions. The extent of CMC reduction in concentrated brines would be even greater. Therefore, it is possible that the onset of borax flotation may also coincide with the formation of hemimicelles.

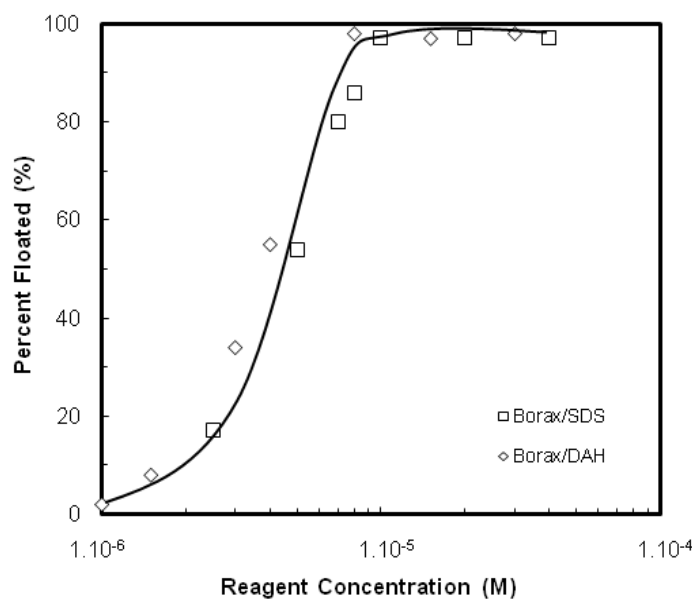


Figure 5. Flotation recoveries of colemanite and borax vs. the concentration of anionic and cationic surfactants at pH 9.3 (Celik et al., 1993).

The most prominent one is Na^+ in the structure of borax. Apart from the effect of monovalent ions in compressing the double layers of minerals, they also modify the bulk water structure and micellization of collectors and consequently enhance surface activity of collectors. There are controversial opinions about the role of monovalent ions in the floatability of minerals. While some assert that monovalent cations and anions depending on their water-breaking and-making structure modify the bulk structure of water and extrapolate the same effect all the way to the surface, others emphasize adsorption of monovalent ions at solid surfaces and their subsequent interaction with water (Clark and Cooke, 1968; Colic et al., 1997; Hancer et al., 2001). The previous results showed that for all boron minerals the potential determining ions are the constituent lattice ions, i.e., $\text{B}_4\text{O}_7^{2-}$ and the counterion, as well as the H^+ and OH^- ions. The addition of SDS and DAH marginally affects the zeta potential of colemanite with pH. Especially, zeta potential of amine adsorbed onto borax revealed an abrupt increase in zeta potentials above critical DAH concentrations. It is generally accepted that monovalent ions are indifferent electrolytes and thus only function in the compression of an electrical double layer; this compression ceases at about 1 M monovalent salt addition where the thickness of the electrical double layer is on the order of the ionic size. Some researchers believe that the electrostatic interactions sharply decay above 0.1 M of salt addition. At monovalent salt levels higher than 0.1 M and especially at 1 M, the electrostatic mechanism may be conveniently ruled out.

Accordingly, smaller, more strongly hydrated ions would produce a larger short-range repulsive force because of the greater energy required to dehydrate the smaller cations (Colic et al., 1997). The only plausible mechanisms that can be proposed under such high ionic strength conditions are ion exchange or hydrogen bonding. Addition of monovalent salts is known to reduce the CMC and consequently dissolve salts of multivalent ion precipitates at lower SDS levels (Celik and Somasundaran, 1988). The precipitation appears to start at 0.1 M salt concentration and undergoes dissolution with increasing of the salt concentration.

2.3 Trona flotation

Trona (sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is the major source of soda ash in the United States. Soda ash, the common name for sodium carbonate, is one of the most widely used raw materials in the U.S. (Kostick, 2004), and the largest use of soda ash is in the production of glass. Since soda ash has a low melting point, the use of soda ash allows silica to be melted at low temperatures and therefore easily handled and formed (Garrett, 1991). This situation accounts for the important dependence that the glass industry has on soda ash production.

The largest known trona deposits in the United States are located in Green River, Wyoming where 14.5 million tons were mined in 2003 and the total estimated value of the domestic soda ash produced was \$800 million (Kostick, 2004). Trona is not so common and significant deposits are found only in a few locations; Africa, China, Turkey, and Mexico. None of these trona resources compare to the vast trona deposit of the Green River Basin in the U.S.

Trona ore consists mainly of trona, including minor undesirable gangue materials a number of double carbonate salts in addition to dolomitic shale, quartz and clays (Garrett, 1991). In the industry, conventional production of soda ash from trona is a complex process with many steps to eliminate the insoluble components of the trona ore. Conventional soda ash production involves the following unit operations; dissolution, clarification, filtration, calcination and crystallization in different order depending on the process design. The insoluble content of the trona ore plays an important role. The insoluble components of the trona ore must be eliminated. In addition production of soda ash has a significant energy demand due to calcination and crystallization operations. In this regard, mining and processing costs, particularly energy costs, are higher than desired and these costs have a significant impact on the cost for production.

With the present industrial practice, there is no particle separation process to remove these insoluble minerals prior to thermochemical processing. Recently, a research at the University of Utah showed that the removal of gangue minerals from trona ore could be accomplished by froth flotation (Ozdemir et al., 2010; Wang et al., 2002). In this current research appropriate conditions for trona flotation technology were established from exploratory bench-scale experiments, and the conditions obtained from the bench scale experiments were also applied to pilot scale flotation tests (Ozdemir et al., 2010).

Trona is a complex salt of sodium carbonate and sodium bicarbonate. Despite many studies regarding the flotation of soluble salts, there is a little information about the flotation of carbonate salts. One research study (Ozcan and Miller, 2002) reports that the flotation of soluble carbonate salts is dependent on their water structure breaking or making properties (Figure 6). It was found that the structure breaking sodium bicarbonate (NaHCO_3) salt can be floated with both 12C anionic and cationic collectors, but the structure making sodium carbonate (Na_2CO_3) salt does not float due to the inability of the collector to break the organized water structure and at the surface of Na_2CO_3 . Also because trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is a structure maker, flotation is generally difficult with 12C collectors. In the trona brine, the structure making character of sodium carbonate dominates and direct flotation of trona with 12C collectors is impossible. These facts support the use of a reverse flotation strategy to float the gangue minerals by flotation and thus produce a trona concentrate.

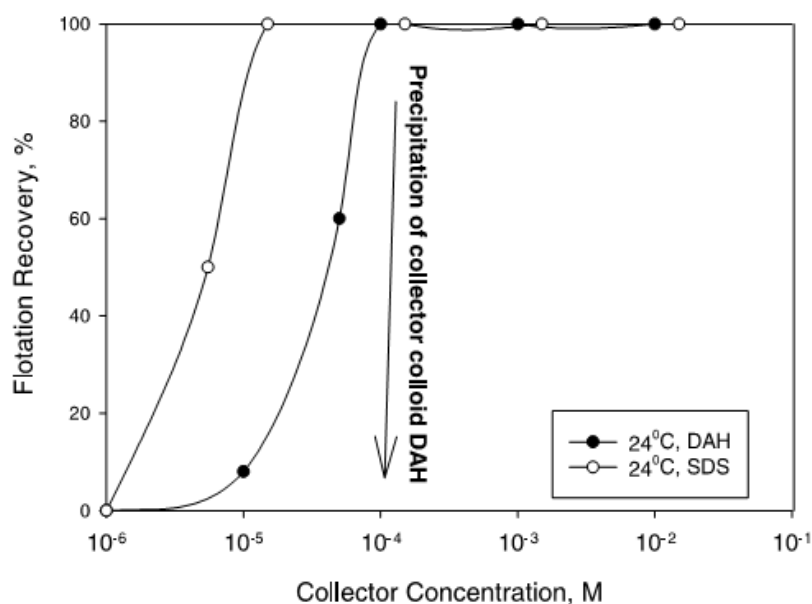


Figure 6. Flotation recovery of the sodium bicarbonate salt as a function of collector concentration at room temperature, pH 8.3 (Ozcan and Miller, 2002).

3. Bulk solution properties of ions in flotation systems

3.1 Viscosity of salt solutions

It has been long established that the dissolved ions in water increase or decrease water-water interactions (Desnoyers and Perron, 1972). Ions of dissolved salts can increase or decrease the solution viscosity. The solution viscosity is an important macroscopic parameter which significantly affects the solid and gas dispersions, the bubble rise velocity and the drainage of both foam and wetting films in flotation. The viscosity of salt solutions is also used often to classify water-soluble salts into structure making (cosmotropes) and structure breaking (chaotropes).

We therefore measure the viscosity of the salt solutions to provide us with information about their structure making/breaking character. For example, Figure 7 shows the relative viscosity values of selected salts as a function of salt concentration. As seen from Figure 1, the salts such as LiCl, NaCl, NaI, LiI and KF generally result in a viscosity greater than 1. However, the salts such as KCl, KI, CsI, RbCl, and KI result in viscosities less than 1. It can be concluded from these results that salts of small ions such as Li⁺, Mg²⁺, F⁻, and Cl⁻ which increase the viscosity of aqueous solutions, are considered structure makers and those salts of large ions such as Cs⁺, Rb⁺, and I⁻ decreasing the solution viscosity are called the structure breaking (chaotropes) (Jiang and Sandler, 2003a; Kaminsky, 1957).

For example, salts such as NaCl increasing the solutions viscosity show the structure making characteristic. However, salts such as KCl decreasing the solution viscosity, show structure breaking character.

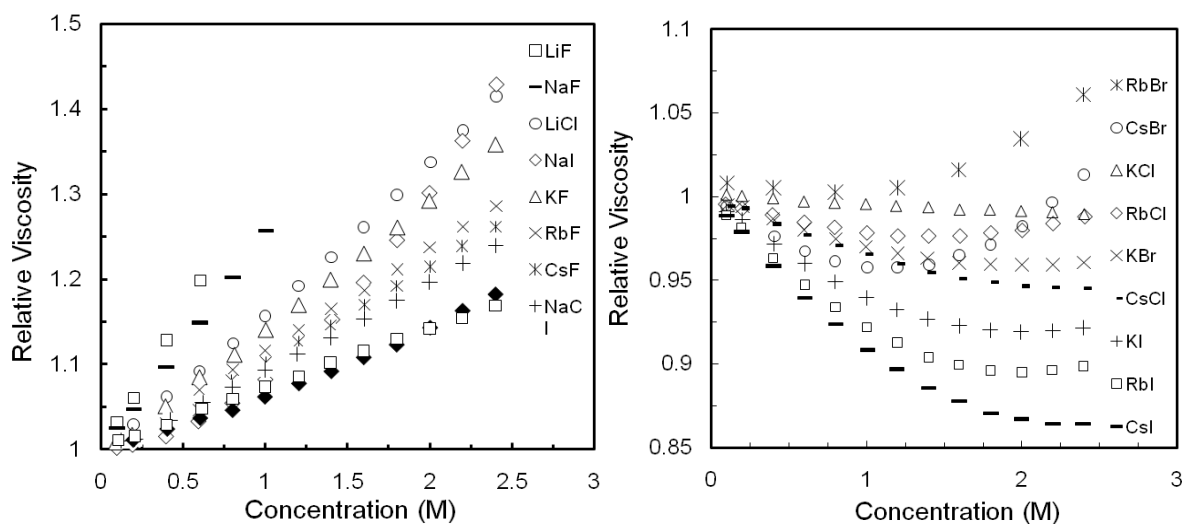


Figure 7. Viscosity (relative to water) of structure making (a) and breaking (b) salt solutions (Hancer et al., 2001).

The solution viscosity was also found to correlate well with the floatability of carbonates and bicarbonates in trona flotation (Ozdemir et al., 2007). For example, Figure 8 shows the viscosity values of carbonate and bicarbonate solutions as a function of salt concentration. The viscosities of the salt solutions increase with increasing salt concentration up to the saturated concentrations. The dependence of the viscosity on concentration for Na_2CO_3 and K_2CO_3 is strong and highly non-linear. The viscosity for NaHCO_3 and NH_4HCO_3 solutions, on the other hand, shows a significantly weaker dependence on salt concentration. These results again reveal that the Na^+ has a stronger structure making effect than K^+ . In fact the lower viscosity for the K_2CO_3 solution may reflect the structure breaking influence of the K^+ ion over the strong structure making effect of the CO_3^{2-} . Since carbonate solutions increase considerably the viscosity of water, Na_2CO_3 and K_2CO_3 , as a general concept, can be classified as strong structure maker salts. Unlike carbonates, bicarbonates, NaHCO_3 and NH_4HCO_3 , only slightly increase the viscosity of their solutions. On this basis, they can be classified as weak structure maker salts. It is interesting to note that carbonates cannot be floated with either DAH or SDS. On the other hand, bicarbonates show high floatability with both collectors (Ozcan and Miller, 2002). The high viscosity values of carbonate salt solutions at saturation could be attributed to the difficulty of floating carbonate salts. In contrast, the lower viscosity of the saturated bicarbonate salt solutions can be responsible for their good floatability. It is very interesting that bicarbonates here are found to be weak water structure makers and therefore expected to hinder the adsorption of collectors on their surfaces. However, their floatability with both cationic and anionic collectors do not agree with the findings of the previous work on alkali halide salts (Hancer et al., 2001). These results suggest that some critical level of structure making can be tolerated for flotation with 12C surfactants. The phenomena occurring at the water–salt interface are complex and the flotation response cannot always be fully described by consideration of just one factor.

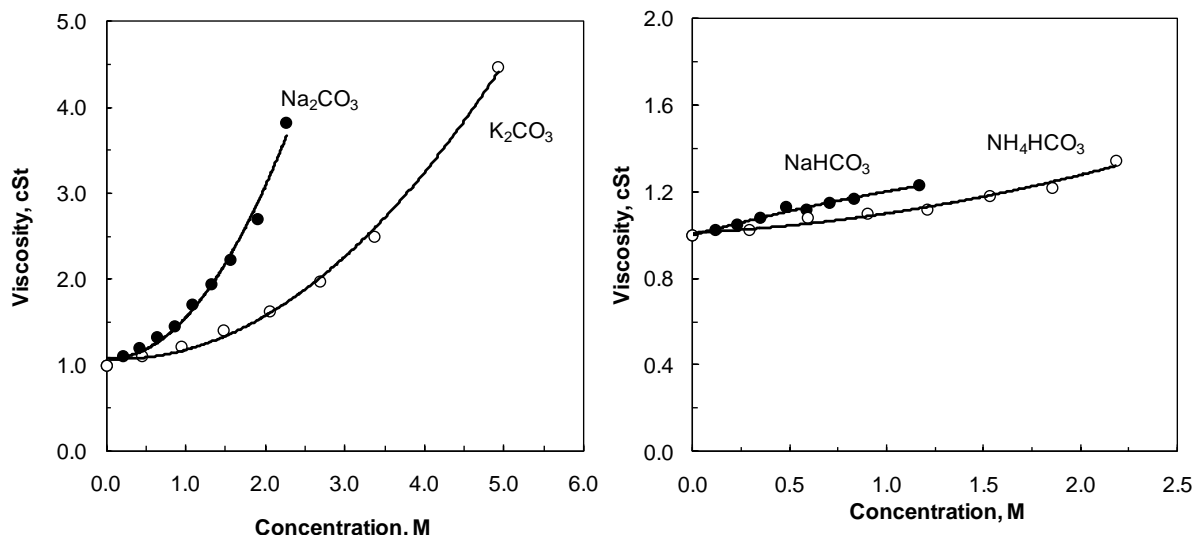


Figure 8. Viscosity of carbonate and bicarbonate solutions as a function of concentration at 23°C (Ozdemir et al., 2007).

3.2 Results of spectroscopy studies

The effect of dissolved ions on water structure at the molecular level can also be determined experimentally by vibrational (IR and Raman) spectroscopy. Vibrational spectra gives direct evidence about the changes in the strength of the hydrogen bonds between water molecules, and therefore reflects the interaction between dissolved salt ions and water molecules (Nickolov and Miller, 2005). Depending on the salt type, the interactions will change (Figure 9). It has been proved that some ions showing structure making effect on water structure increased the width of the O-D band and shifted its peak to lower wavenumbers while others showing structure breaking effect on water structure decreased the width of the O-D band and shifted its peak to higher wavenumbers (Nickolov and Miller, 2005).

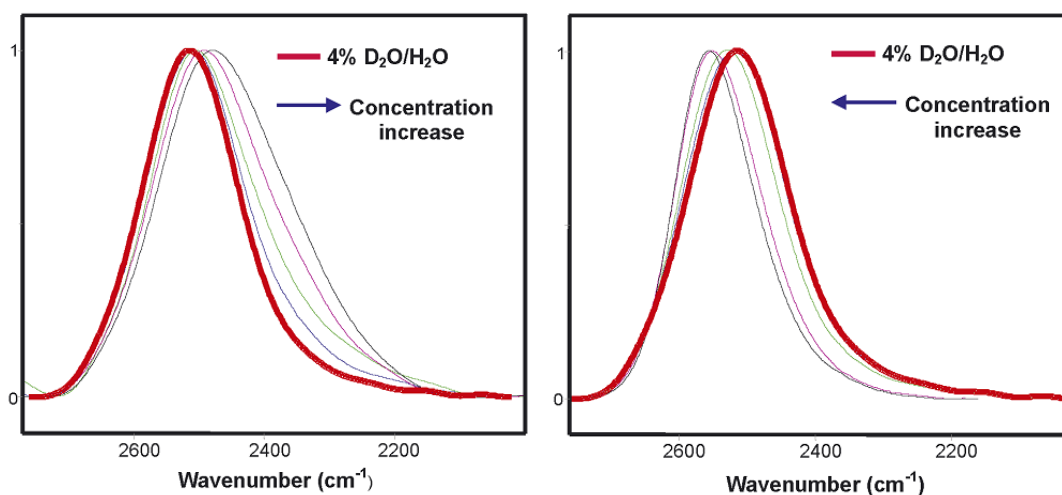


Figure 9. O-D stretching band spectra of solutions of KF (left) and KI (right) in 4w% D₂O in H₂O mixtures at different salt.

The results with carbonates and bicarbonates (Figure 10) also showed a similar trend in that the water structure was significantly affected with increasing sodium carbonate concentration. On the other hand, the water structure in the presence of NaHCO_3 increased only slightly (Ozdemir et al., 2007).

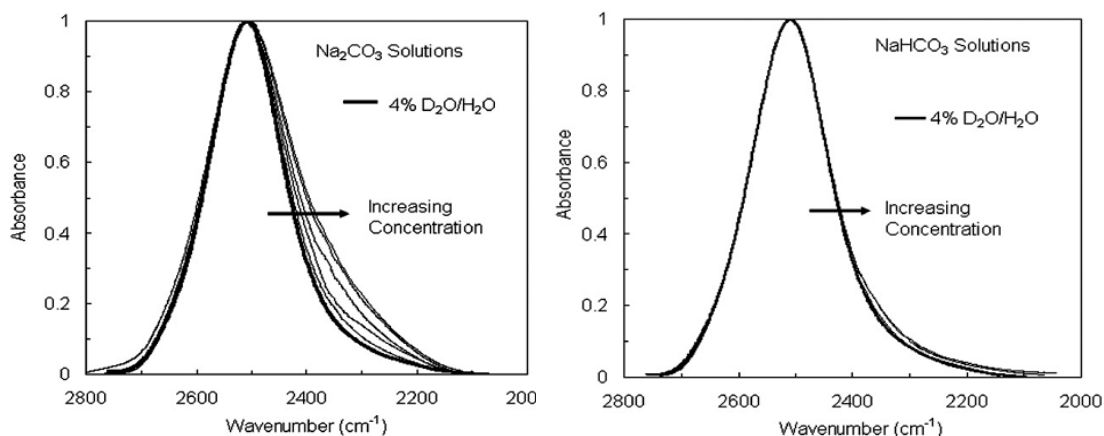


Figure 10. OD stretching band in carbonate and bicarbonate solutions containing 4% D_2O as at different salt levels.

3.3 Results of molecular dynamics (MD) simulations

Molecular dynamics (MD) simulation is a fundamental tool which can be used to explore water/water, water/ion and ion-ion interactions, and to elucidate the influence of salts on the dynamic properties of brine solutions (Berendsen, 1988; Berendsen and Van Gunsteren, 1984; Dang, 1992a; Haile, 1997). In the past decade, much research has been devoted to the study of water structure, as well as the dynamic and thermodynamic characteristics of electrolyte solutions (Chowdhuri and Chandra, 2001; Chowdhuri and Chandra, 2003; Dang, 1992b; Dang, 1994; Dang, 1995; Dang and Smith, 1993; Dang and Smith, 1995; Koneshan et al., 1998a; Koneshan et al., 1998b; Lee and Rasaiah, 1994; Lee and Rasaiah, 1996; Lynden-Bell and Rasaiah, 1996; Smith et al., 1997; Uchida and Matsuoka, 2004). Also efforts have been made to characterize the energy parameters of various ions (Dang, 1992a; Dang, 1992b; Smith and Dang, 1994a; Smith and Dang, 1994b; Smith et al., 1997). The thermodynamics of solvation of simple ions as a function of their size, charge, and charge inversion, have been studied by MD simulation at infinite dilution extensively (Koneshan et al., 1998b), and different types of hydration have been identified and discussed in relation to the energy and entropy of solvation. Systematic investigations by MD simulation of concentrated alkali halide solutions with respect their effect on water structures and the physicochemical properties of the solutions are limited.

3.3.1. Water structure

MD simulations of LiCl , RbCl , and CsI solutions have revealed that water structure is dependent on the ions present in the solution as shown in Figure 11, which summarizes the effect of different ions and their concentrations in solution on water/water coordination. In pure water, water molecules form dynamic tetrahedral networks with average coordination of 4.5. When Li^+ ions are present, due to their large local electric field, water molecules are

tetrahedrally coordinated and tightly held around ions, and form hydrophilic hydration shell as shown in Figure 12a. As more Li^+ ions are present, the number of water molecules tetrahedrally bonded with Li^+ ions increases accordingly and one direct result is the water/water coordination number increases with salt concentration due to water molecules are pulled together by Li^+ ions.

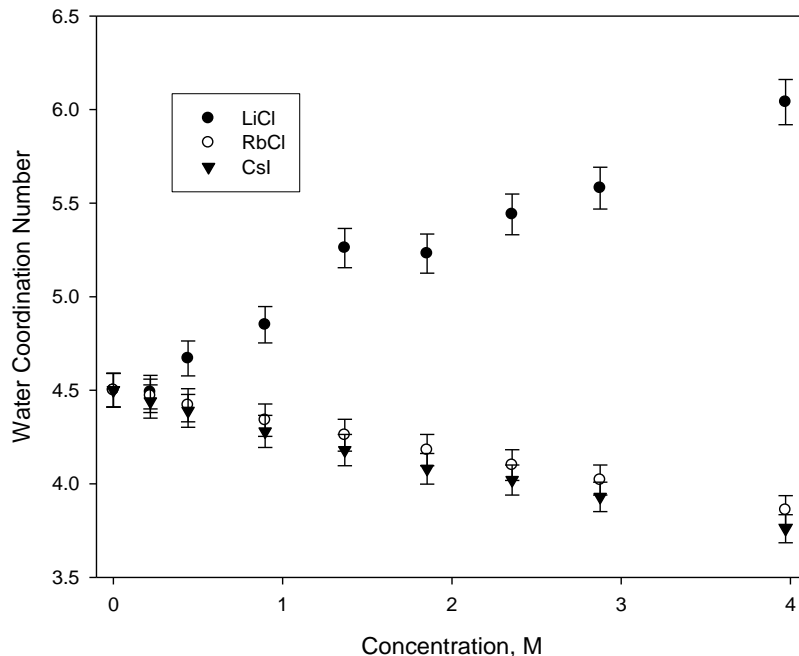


Figure 11. The first shell water/water coordination numbers in different salt solutions against solution concentration (Du et al., 2007a).

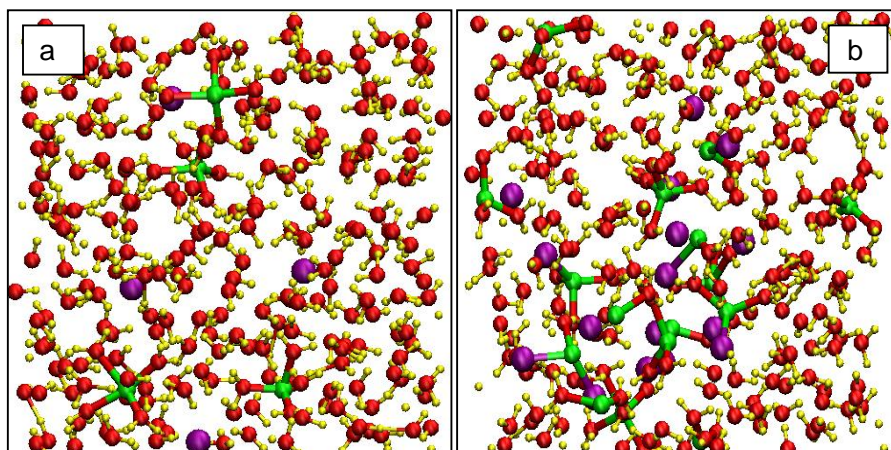


Figure 12. Snap shot from MDS of 0.9 M LiCl solution (a) and 3.97 M LiCl solution (b). (Red - oxygen atom in water, Yellow - hydrogen atom, Purple - Cl^- , and Green - Li^+ .) Each Li^+ is tetrahedrally bonded with four water molecules at low concentration as seen in Figure 12a.

When the solution becomes concentrated, some water molecules in the Li^+ tetrahedral hydration shell are replaced by Cl^- , forming direct cation/anion pairing as illustrated in Figure 12b (Du et al., 2007a).

As the solution becomes more concentrated, some of the water molecules participating in the Li^+ ion hydration shell are replaced by negatively charged Cl^- ions, as shown in Figure 12, hence, the hydration number of Li^+ ions decreases as the solution concentration increases. On the other hand, the water molecules in the Li^+ tetrahedral hydration shell are counted into the hydration shell of Cl^- ion. Therefore, the larger the hydration number of the Cl^- ions increases with solution concentrations.

For larger cations such as Rb^+ and Cs^+ , the size of the hydration shell increases accordingly, and is larger than that of the pure water cluster. Similarly, owing to their large size, the Cl^- and I^- hydration shells are much larger than that of the pure water cluster. For very large cations such as a Cs^+ ion, the local electric fields at the ion surface have decreased significantly, and behave more like uncharged particles (Koneshan et al., 1998b). Hence, as the size of the cation increases, the dominating electrostatic hydrophilic hydration of small ions is gradually replaced by hydrophobic hydration of large ions where hydrogen bonded water molecules form a disordered cage surrounding the ions as can be seen in Figure 13a.

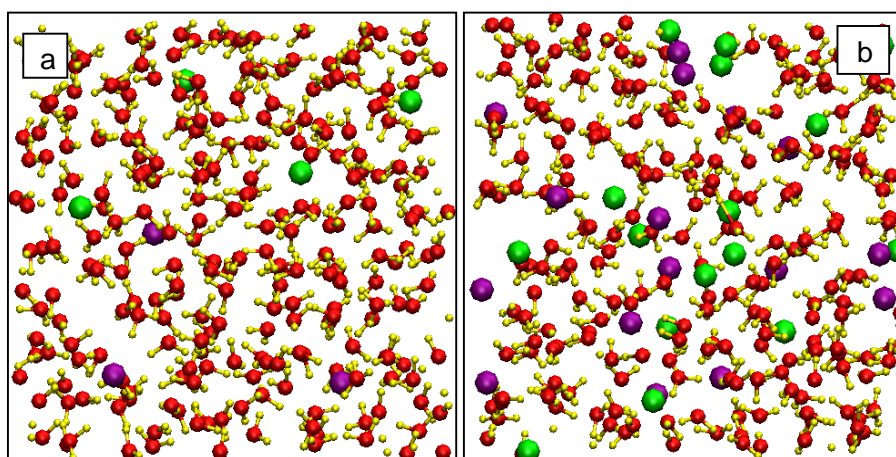


Figure 13. Snap shot from MDS of 0.9 M CsI solution (a) and 3.97 M CsI solution (b). (Red - oxygen atom in water, Yellow - hydrogen atom, Purple - I^- , and Green - Cs^+ .) Water molecules form hydrophobic cages around cations, and stable hydration shells around anions.

At high solution concentration, cations and anions pair up minimizing the number of water molecules in the primary hydration shell around ions (Du et al., 2007a). For water molecules composing the cages, because one position has been taken by these large ions, only three other water molecules can be hydrogen bonded to them and counted as primary waters coordination, thus, the water/water coordination number of these cation bonded water molecules is less than that of pure water cluster. As more ions are in the solution, more water molecules will be around ions, and consequently, the water/water hydration number decreases monotonically with salt concentrations. When hydrophobic hydration dominates, water molecules are loosely bonded to the ion and the radius of the primary hydration shell is large, allowing more water molecules to be accommodated. As the number of ions increases in the solution, there will be fewer water molecules available to complete the cages around ions, and the cations and anions will pair up to include less water molecules in their hydration shells which are fragile and may break, as observed from Figure 13b.

3.3.2. Cation/anion interactions

The cation/anion coordination number as a function of salt concentration is summarized in Figure 14, where both the primary and secondary coordination numbers are presented.

Generally speaking, independent of ion species, both the primary and secondary coordination number between cation and anion increases when the salt concentration increases. Specifically, for the Li^+/Cl^- combination, an increase of the secondary coordination number, which is the interaction of hydrated or solvent separated ions, is much more significant than an increase of the primary coordination number, which is the naked ion-ion interaction. In contrast, for the Cs^+/I^- combination, the primary coordination increases much more significantly with concentration. And for the Rb^+/Cl^- combination, the change in the coordination number for both the primary and the secondary shells are almost of the same magnitude. When Li^+ ions are in the solution, due to the strong local electric fields, water molecules are tightly bonded by Li^+ ions, excluding the direct contact with Cl^- ions. When a large number of ions are in the solution, there is competition between ion/water and ion/ion interactions. Because hydrophilic hydration of Li^+ ions dominates, driven by minimization of system energy, the coordination number between hydrated ions increases more significantly relative to the direct ion/ion contact. For larger ions such as Cs^+ ions, loose hydrophobic hydration shells are formed around these ions. On the other hand, water molecules try to keep their integrity as pure water clusters. Because the direct cation/anion interaction, which will lead to fewer water molecules participating in the hydration shells is energetically more favorable, the primary coordination number increases faster as a function of salt concentration. For the intermediate ion combination (Rb^+ and Cl^-), the ion/water and the ion/ion interactions are in close competition.

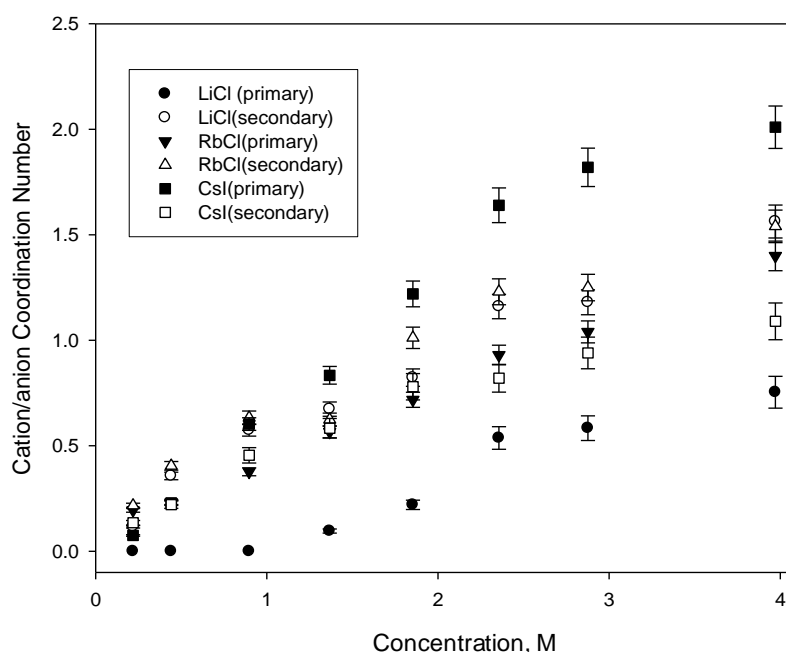


Figure 14. The coordination number of naked cation/anion pairs (direct cation/anion contact) and hydrated cation/anion pairs (a layer of water between cation/anion pair) in different salt solutions for various solution concentrations (Du et al., 2007a).

3.3.3. Dynamic properties

MD simulation has concluded that ion size influences the mobility of water molecules in the solution. When small ions such as Li^+ are present, the mobility of water molecules in both the ion hydration shell and the water-only clusters decreases as a function of salt concentration. Small ions such as Li^+ strongly interact with water molecules in the hydration shell and therefore, significantly confine the movement of water molecules in the primary water shell, resulting in a substantially longer residence time.

In contrast, for solutions containing large ions (CsI and RbCl), the ion/water electrostatic interaction does not contribute significantly to immobilize the water molecules. Consequently, the residence time of water molecules do not show a substantial change with solution concentration. For large ions such as Cs^+ , Rb^+ , and I^- , the local electric fields are weak as discussed earlier, and water molecules in the primary hydration shell are more loosely bonded to them. Thus they are more mobile and the residence time of water is shorter.

The changes of residence times support the observations of self-diffusion coefficients of particles as a function of salt concentration as shown in Figure 15, which suggests that when Li^+ ions are present, the diffusion coefficients of water molecules in the solution decrease significantly with salt concentration, and when Cs^+ and I^- ions are present, there is no significant change of the water diffusion coefficients with salt concentration.

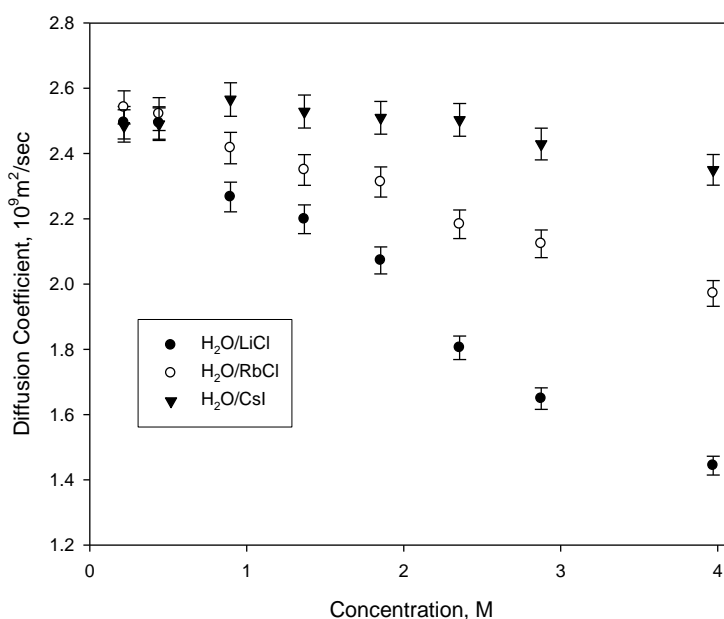


Figure 15. Self-diffusion coefficient of water molecules in water clusters for various solution concentrations (Ref).

3.3.4. Viscosity

The viscosities calculated from our MD simulations of brine solutions as a function of solution concentration are shown in Figure 16. As expected, the size of the ions has a significant influence on the viscosity of the solution. When small ions are present (LiCl solution), the system shear viscosity increases monotonically with solution concentration. As the ion size increases (RbCl solution), the system viscosity shows very weak dependence on the solution concentration. Further increasing in ion sizes (CsI solution), leads to an obvious decrease of viscosity as a function of solution concentration. This variation of solution viscosity as a function of ion size and solution concentration has also been observed experimentally by several research groups (Hancer et al., 2001; Jiang and Sandler, 2003b), so our simulations show the same trends.

In LiCl solution, Li^+ ions interact strongly with either water molecules or corresponding anions, and form stable tetrahedral structures, which contribute substantially to a “sticker” system. Though Cl^- ions, due to their large size, do not form strong bonds with water molecules; the influence of cations is dominating. Consequently, the mobility of the solution will decrease, and system shear viscosity, which describes mobility macroscopically, will increase. The higher the solution concentration, the more significant role the Li^+ ions play, and

the higher the viscosity. In contrast, when large ions (Cs^+ and I^-) are presented in the solution, loose hydrophobic shells were formed around those ions, and the ion/water interaction is not as strong as water/water interaction, accounting for the decrease in the system shear viscosity.

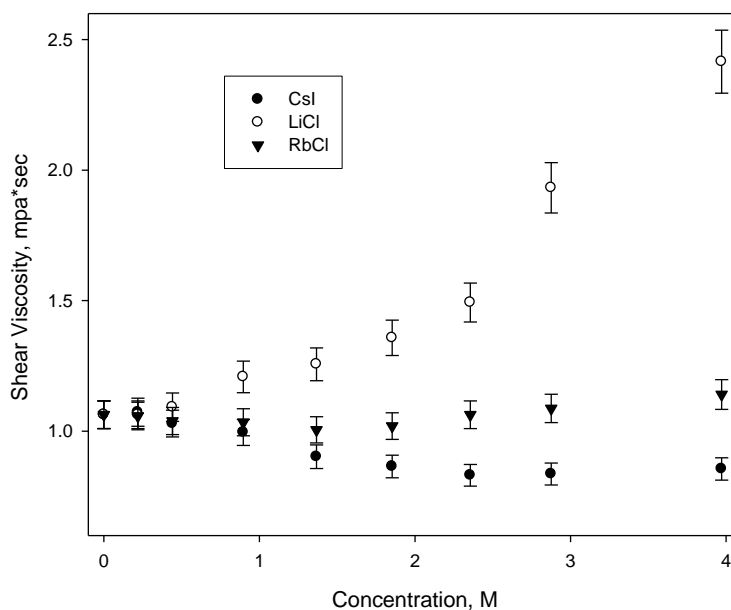


Figure 16. Variation of system shear viscosity with solution concentration (Du et al., 2007a) Is there any graph showing experimental and predicted viscosities?

The change of system viscosity with solution concentration as determined from MD simulation in this study successfully compliments the experimental results reported in the literature (Dang and Smith, 1995; Koneshan et al., 1998b), and provides an in-depth understanding regarding the variation of viscosities as a function of ion sizes and salt concentrations from a molecular perspective. For LiCl solutions, the system viscosity increases monotonically with salt concentration due to the strong ion/water interactions in the solution. As the ion size increases e.g. the case of RbCl, hydrophobic hydration becomes dominating, and leads to negligible variation of system viscosity with salt concentration. Further increase in the ion size to Cs^+ and I^- revealed a noticeable decrease of system viscosity as a function of salt concentration. The excellent agreement between the simulation results and the experimental results for the variation of viscosity with ion size and concentration provides future information to phenomenologically describe the behavior of particles in alkali halide solutions.

4. Effect of ions at air-water interfacial properties

4.1 Surface tension

The presence of salt ions in solution not only changes the properties of solid-water interfaces but also the air-water interfaces, thus additionally effecting the interaction between particles and bubbles during flotation. It is important to understand how these electrolytes behave at the interfaces. As seen in Figure 17, most of the electrolytes increase the surface tension of water with increasing salt concentration (Weissenborn and Pugh, 1996). An increase in surface tension in the presence of electrolytes has been explained by negative adsorption of ions at air-water interface, however, some electrolytes such as HCl, HNO_3 , etc., decrease the surface tension of water so that they positively adsorb at the air-water interface.

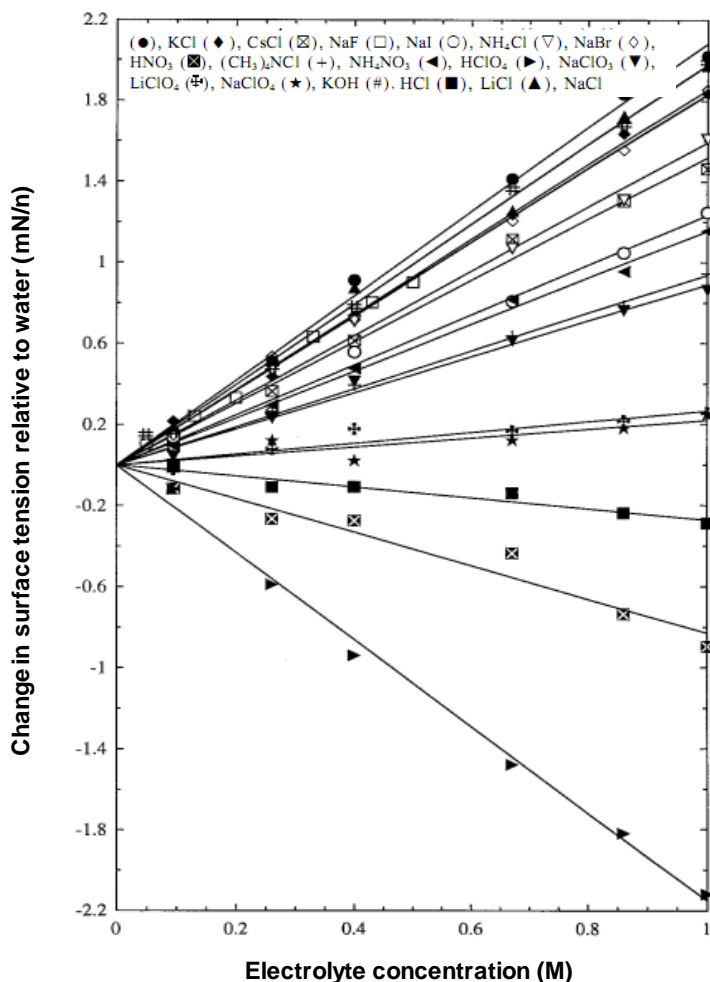


Figure 17. Effect of electrolyte on the change in surface tension relative to water for 1:1 electrolytes (Weissenborn and Pugh, 1996).

As mentioned before, the flotation of soluble salts must be carried out in their saturated solutions. An interesting study about the surface tension of selected salts (NaCl, KCl, KI, KNO₃, NaF, and K₂SO₄) as a function of concentration up to their solubility limit showed that the surface tension of the aqueous solutions increases with increasing salt concentration up to their saturation points (Figure 18). It is interesting to note that the solubility of these salts play a significant role on their surface tension values with a more soluble salt giving higher surface tension at a given level of saturation (Ozdemir et al., 2009b). As mentioned before, NaCl and NaF are structure makers. On the contrary, KCl, KI, KNO₃, and K₂SO₄ are structure breaker salts. It is evident that there is no correlation between the surface tension of these salts and their structure making and breaking effect on the flotation response.

The surface tension experiments with carbonate (Na₂CO₃ and K₂CO₃) and bicarbonate (NaHCO₃ and NH₄HCO₃) solutions also showed the same trend that while carbonates significantly increases the surface tension as the salt concentration increase, the increase in the surface tension of NaHCO₃ and NH₄HCO₃ solutions is not significant (Figure 19).

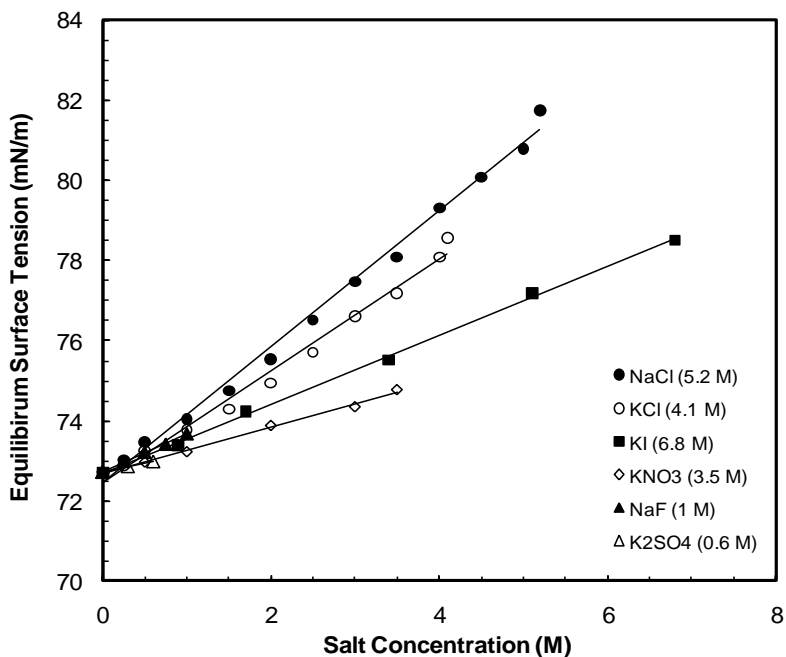


Figure 18. Surface tension of salts versus concentration up to the point of saturation at 25°C (Ozdemir et al., 2009b).

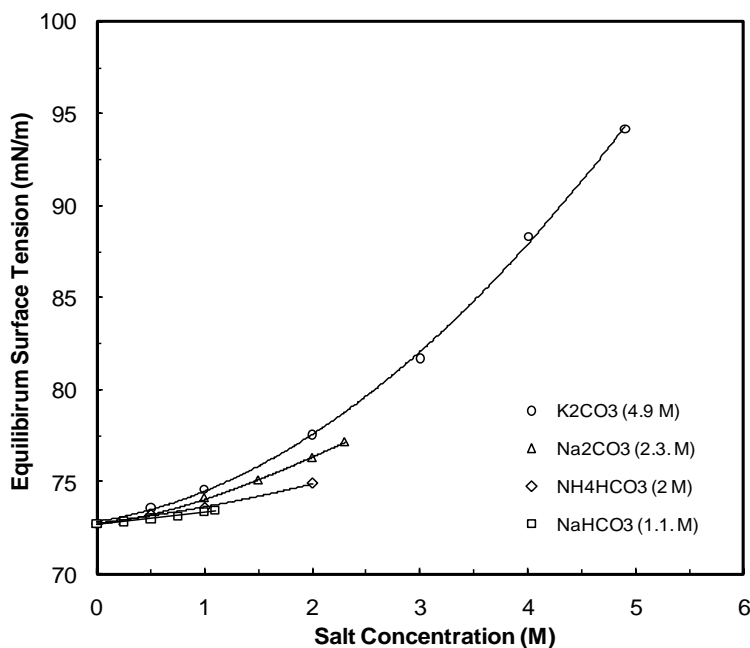


Figure 19. Surface tension of carbonate and bicarbonate salts versus concentration up to the point of saturation at 25°C (Ozdemir et al., 2006).

4.2 Sum-frequency vibrational spectroscopy (SFVS)

SFVS is a powerful nonlinear optical technique for investigating molecules at the salt water-air interfaces. Figure 20 shows the SFVS spectra of pure water, saturated NaHCO_3 and saturated Na_2CO_3 solutions. The spectral feature of pure water as observed in the SFVS

spectrum is similar to the previous studies at the same air/water interface (Gopalakrishnan et al., 2005; Mucha et al., 2005; Shen and Ostroverkhov, 2006). Generally, three OH stretching frequencies at ~ 3200 , 3400 , and 3700 cm^{-1} characterize the OH vibrations in water. The spectrum of pure water indicates that the interfacial water structure consists of a partially ordered and a partially disordered hydrogen bonding network. Compared to the spectrum of pure water, the intensity of the “ice-like” peak at 3200 cm^{-1} slightly decreases in the spectrum of the NaHCO_3 solution, but significantly increases (\sim by a factor of 4) in the Na_2CO_3 solution. The increase in the SFVS intensity suggests that more polar-ordered hydrogen bonding water network is formed at the surface of the Na_2CO_3 solution. In contrast, at the surface of the NaHCO_3 solution, a weakly ordered water structure is suggested. These results are in good agreement with the surface tension of these salts.

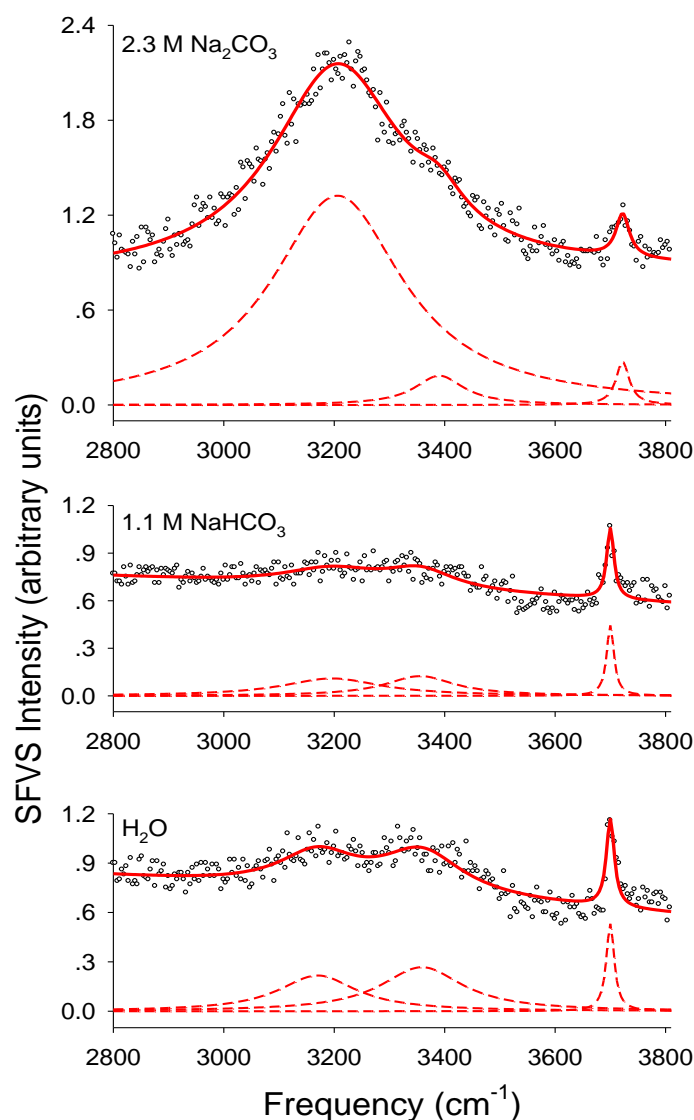


Figure 20. The SFVS spectra for pure water, saturated sodium bicarbonate solution and saturated sodium carbonate solution in the O-H stretching region at the air-liquid interfaces at 23°C (Du et al., 2008).

4.3. Ion-specific effect on froth stability and thin liquid films (TLF)

4.3.1. Bubble coalescence in salt solutions

The density of the bubbles in froth is decisive for flotation. Therefore, the effect of the inorganic salts on the froth stability was studied for the last four decades (Christenson and Yaminsky, 1995; Craig, 2004; Craig et al., 1993a; Craig et al., 1993b; Deschenes et al., 1998; Duineveld, 1998; Henry et al., 2007; Kim et al., 1990; Kim and Lee, 1988; Kumar and Ghosh, 2006; Marrucci and Nicodemo, 1967; Nicodemo et al., 1972; Pashley and Craig, 1997; Pugh et al., 1997; Tsang et al., 2004; Vrtovsek et al., 1989; Weissenborn and Pugh, 1995a; Weissenborn and Pugh, 1995b; Yu and Jer, 1983). It was established that a number of inorganic salts inhibit the bubble coalescence above certain critical (transition) concentration in gas dispersion as compared to other salts with no effect (Christenson and Yaminsky, 1995; Craig, 2004; Craig et al., 1993a; Craig et al., 1993b; Deschenes et al., 1998; Duineveld, 1998; Henry et al., 2007; Kim et al., 1990; Kim and Lee, 1988; Kumar and Ghosh, 2006; Marrucci and Nicodemo, 1967; Nicodemo et al., 1972; Pashley and Craig, 1997; Pugh et al., 1997; Tsang et al., 2004; Vrtovsek et al., 1989; Weissenborn and Pugh, 1995a; Weissenborn and Pugh, 1995b; Yu and Jer, 1983).

Thermodynamically, gas dispersion is very unstable system tending to decrease its total surface by multiple bubble collision. Physically, gas dispersion in the dynamic conditions of flotation is complex system with given rheology (Duineveld, 1995; Duineveld, 1998; Kim and Lee, 1988; Kumar and Ghosh, 2006; Yu and Jer, 1983) (approach velocity, bubble sizes, surface tension, etc.) and surface forces between the bubbles (Derjaguin and Landau, 1941; Verwey and Overbeek, 1948). In this context, inhibition of the bubble coalescence can occur by decreasing the surface tension (this enhances the disperse-ability of the gas phase into the liquid medium), by increasing the approach velocity of the bubbles (making them to bounce after their contact) and by increasing the electrostatic repulsion between the bubbles (by adsorption of ionic surfactants). The adsorption of surfactants on gas/liquid interface decreases the surface tension significantly and consequently inhibits the bubble coalescence. In contrast, the inorganic electrolytes increase the surface tension and suppress any electrostatic repulsion between the bubbles. Therefore, they should promote the bubble coalescence. However, most of the inorganic electrolytes stabilize bubbles above certain concentrations (Christenson and Yaminsky, 1995; Craig, 2004; Craig et al., 1993a; Craig et al., 1993b; Deschenes et al., 1998; Henry et al., 2007; Kim et al., 1990; Marrucci and Nicodemo, 1967; Nicodemo et al., 1972; Pashley and Craig, 1997; Tsang et al., 2004; Vrtovsek et al., 1989; Weissenborn and Pugh, 1995b) at which the electrostatic repulsion between the bubbles is totally suppressed (Craig et al., 1993a; Craig et al., 1993b; Pashley and Craig, 1997). In addition, the bubble size appears to be important for the rate of bubble collision (Tsang et al., 2004). Some salts do not have an effect on the bubble coalescence at any concentration.

It was observed that the density of bubbles in gas dispersion correlates well with certain combinations of the cation and anion of the salt (Craig et al., 1993a; Craig et al., 1993b; Pashley and Craig, 1997). An empirical rule was established (Craig et al., 1993a; Craig et al., 1993b; Pashley and Craig, 1997) according to which the ions are classified as α and β ions. This rule postulates that the effect of the salt is controlled by proper combination of ions: salt consisting of α cation and α anion or β cation and β anion inhibit the coalescence of the bubbles, while salts consisting of mixed α and β ions have no effect.

It was believed that Marangoni effect on the surfaces of bubbles in contact impedes their coalescence by the Gibbs elasticity of the adsorption layer of the inorganic salts (Chan and Tsang, 2005; Prince and Blanch, 1990a; Prince and Blanch, 1990b), however this hypothesis was found recently inconsistent (Craig, 2004). An alternative way to explain the slower coalescence of bubbles suggested recently (Marcelja, 2006), is the electrostatic repulsion

between the bubbles. Their surface potential is generated by specific spatial distribution of anions and cations in the vicinity of the air/water interface. This ionic distribution occurs at distance less than 1 nm from water/air interface. Therefore, bubbles at distance larger than 2 nm do not interact electrostatically due to the very small inverted Debye length (less than 1 nm). In addition, significant van der Waals and short-ranged spinodal cavitation attraction forces (Stevens et al., 2005) act between the bubbles at distance less than 10 nm. Another way to explain the prohibited coalescence of bubbles is that some combinations of ions can decrease the surface mobility of the gas/liquid interface thus immobilizing the surfaces of the bubbles however this hypothesis was refuted recently (Henry et al., 2008). This ion-specific effect does not correlate with the increment of the surface tension of water/air interface (Henry et al., 2007) as well.

Experiments with sum-frequency generation vibrational spectroscopy (SFG) and molecular dynamic simulations report (Du et al., 2008) that some salts in their brine solutions make the water structure network close to the water/air interface more compact while other salts make it less compact as compared to pure water. Thus the salts were classified as structure makers and structure breakers. However, these findings do not correlate with the ion-specific effect on bubble coalescence (Tables 2) (Craig et al., 1993a) as well. As seen from Tables 2 there are structure makers and structure breakers (e.g. NaCl and KCl) both of which inhibit the bubble coalescence.

Table 2. Effect of salts on the bubble coalescence (Craig, 2004)

	Cations	H ⁺	Li ⁺	Na ⁺	K ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	NH ₄ ⁺	(CH ₃) ₄ N ⁺	(CH ₃) ₄ NH ⁺	(CH ₃) ₄ NH ₂ ⁺	(CH ₃) ₄ NH ₃ ⁺
Anions	Type	β	α	α	α	α	α	α	α	β	β	β	β
OH ⁻	α	×		✓	✓								
Cl ⁻	α	×	✓	✓	✓		✓	✓		×	×	×	×
Br ⁻	α	×		✓	✓	✓							
NO ₃ ⁻	α	×	✓	✓	✓			✓					
ClO ₃ ⁻	β			×									
ClO ₄ ⁻	B	✓		×			×		×				
CH ₃ COO ⁻	β	✓		×	×	×	×	×	×				
SO ₃ ²⁻	α	×		✓			✓			✓			
(COO) ₂ ²⁻	α	×			✓								

Combining rules:

αα or ββ salts inhibit bubble coalescence (✓)

αβ or βα salts do not inhibit bubble coalescence (×).

Therefore the ion-specific effect could be related to the bulk properties of the salt solutions. Interestingly, it was reported in the literature (Pugh et al., 1997; Weissenborn and Pugh, 1995b) that inorganic salts reduce the solubility of oxygen. Correlation between the solubility of oxygen and ion-specific effect on the bubble coalescence can be found (Pugh et al., 1997; Weissenborn and Pugh, 1995b). When existing, the ion-specific effect on bubble coalescence can be evaluated by the transition concentration of salt, beyond which the effect appears. The smaller the transition concentration, the stronger the ion-specific effect is. The solubility of oxygen depends on the concentration of salt as an exponential decay function (Weissenborn and Pugh, 1996). The larger the absolute value of exponential decay coefficient, the smaller the solubility of oxygen is. Figure 21 shows correlation between the decay coefficient and the transition concentration of salts. The lower the solubility of oxygen the stronger the inhibition of the bubble coalescence is. The salts with multivalent ions have strongest effect. Unfortunately, data on solubility of oxygen in the presence of different salts are scarce. These last findings give a hope that the ion-specific effect could be understood in near future. All of the experiments on bubble coalescence were performed with bubble columns, where the multiple gas bubbles were generated by passing purified air or nitrogen

through an orifice or through a porous surface such as a sintered glass disk. Therefore, the experimentally established rate for bubble coalescence is a statistical value based on the observation of multiple bubble collisions. There are no systematic literature data showing the behavior of foam film between two bubbles in contact of highly concentrated salt solutions. Such a study has been conducted recently by Karakashev et al (Karakashev et al., 2008). Micro-interferometric method of Scheludko has been utilized for studying foam films with two pairs of active (NaCl and LiCl) and inactive (NaClO₃ and NaAc) salts. The foam films have been studied in open and closed cells. In open cell the foam film is in contact with the air of the lab, hence it can evaporate. In a closed system the foam film is in contact with saturated water vapors and, hence it cannot evaporate. According to the DLVO theory all the foam films should drain until rupture despite the kind of the salt. Indeed, in the case of open cell: the foam films prepared from the NaAc and NaClO₃ solutions thinned until rupture; the foam films prepared from dilute (below 0.1 M) NaCl and LiCl salt solutions drained until rupture as well; however, the foam films prepared from concentrated NaCl and LiCl salt solutions were relatively stable and exhibited significant dynamics (see Fig. 22). Thus some salts stabilize the foam films, while others not. This is deviation from the prediction of the DLVO theory and ion-specific effect.

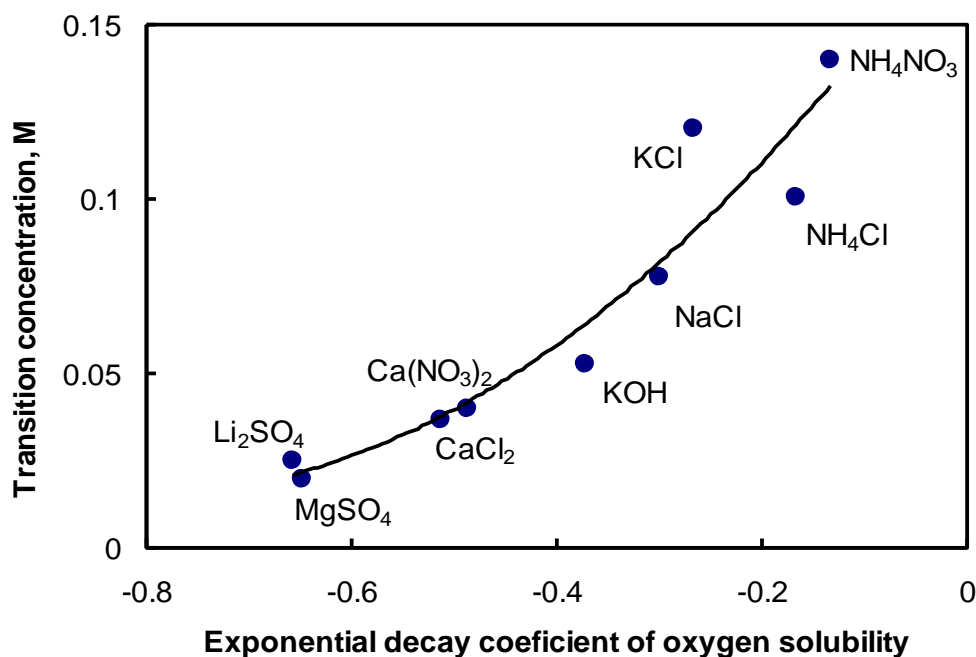


Figure 21. Correlation between the transition concentration exponential decay coefficients for oxygen solubility (Weissenborn and Pugh, 1996).

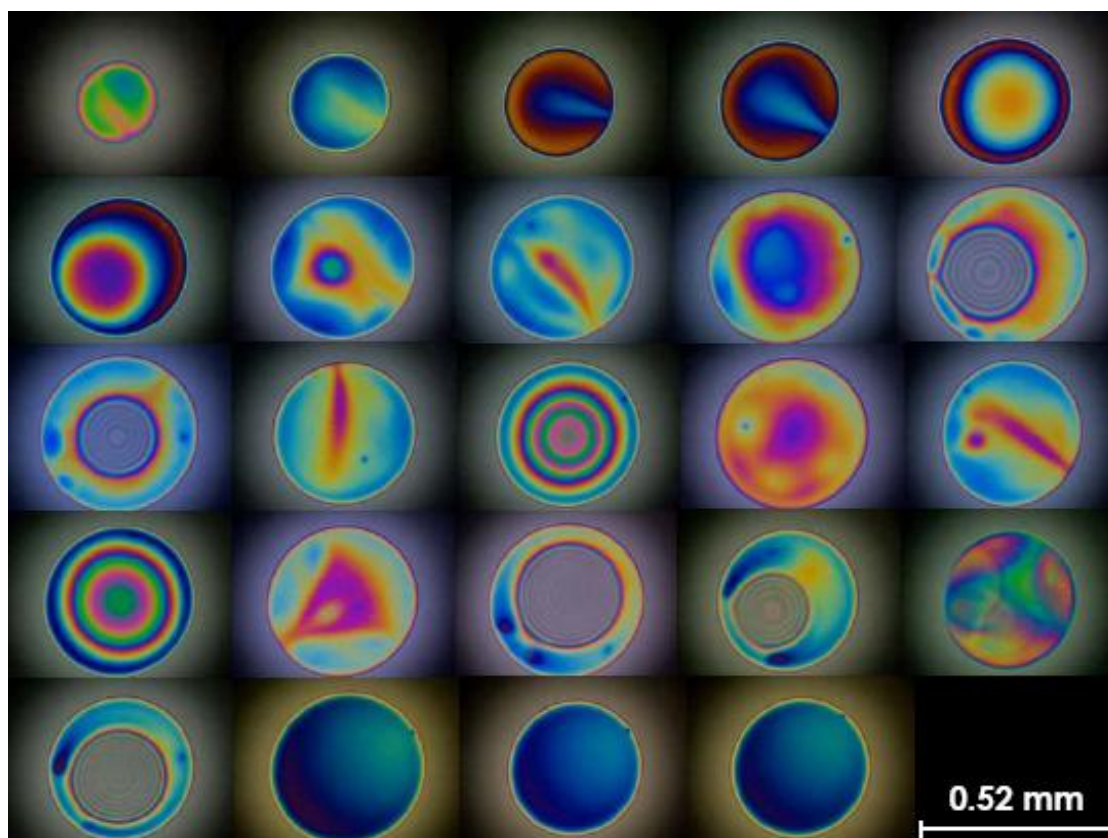


Figure 22. Evolution with significant dynamic surface corrugations of a 4 M NaCl foam film, shown at a time interval of 5 s (from the top left to bottom right corner).

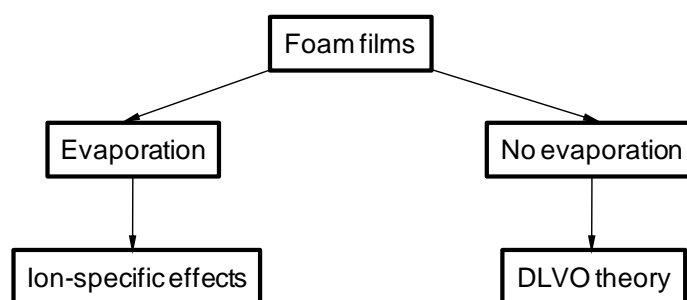


Figure 23. The ion-specific effects in thin foam films of concentrated salts observed under special conditions of evaporation and saturation.

In the study of the drainage and stability of foam films of concentrated salt solution using the Scheludko cell technique (Karakashev et al., 2008) it was observed that in the case of closed cell saturated by vapour of the salts all the foam films drained until rupture thus exhibiting short lifetime. Hence, they followed the prediction by the classical colloidal theory known as the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory (Nguyen and Schulze, 2004). The ion-specific effects in thin liquid films were observed when the films were in contact with unsaturated environment of the Scheludko cell open to the ambient atmosphere and might undergo fast evaporation. These interesting observations of the effect of saturation by salt vapour and the evaporation of salt solutions from the foam films are illustrated in Fig. 23.

4.4 Molecular dynamics simulations

4.4.1. Brine/air interface

A MDS snapshot of the Na_2CO_3 solution and a corresponding number density distribution plot is shown in Figure 24. It is evident from the snapshot that, both sodium and carbonate ions are excluded from the air/water interface due to significant hydration of these ions. The particle number density plot further reveals the deficiency of ions at the air/water interface over a region extending to about 10 Angstroms in thickness, showing a strong negative adsorption for both Na^+ ions and CO_3^{2-} ions, which accounts for the increased surface tension reported previously (Andersson et al., 2007; Gopalakrishnan et al., 2005; Jungwirth et al., 2006; Jungwirth and Tobias, 2002; Jungwirth and Tobias, 2006; Thomas Jennie et al., 2007) and will be further discussed later. Similar MD simulation observations have also been reported regarding Na_2SO_4 solutions (Gopalakrishnan et al., 2005).

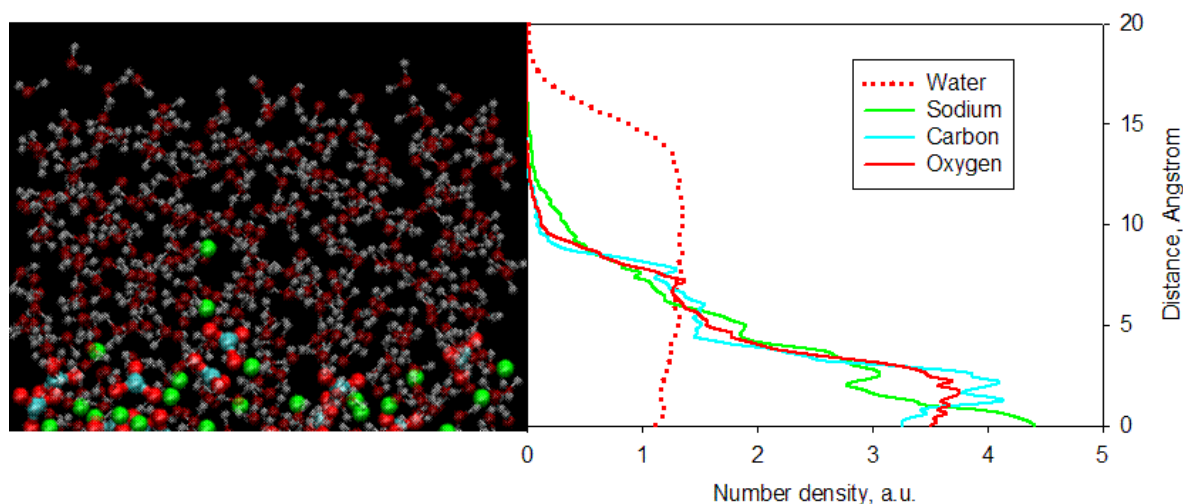


Figure 24. Snapshot of aqueous sodium carbonate solution (2.0 M) (left) and particle number density distributions along surface normal (right). The color representations are as follow: Cyan-Carbon, Green-Sodium, Red-Oxygen, and White-Hydrogen (Du et al., 2008).

In contrast, for the NaHCO_3 solution shown in Figure 25, HCO_3^- ions occupy a portion of the air/water interface due to some affinity of HCO_3^- ions for the air/solution interface. The obvious HCO_3^- ion number density peak at the interface suggests that the presence of bicarbonate ions is energetically favorable. As might be expected, the Na^+ ion peak follows the HCO_3^- ion peak in order to satisfy the cation/anion coulombic interactions. However, the concentration of sodium and bicarbonate ions at the interface is still lower than in the bulk solution, suggesting a slightly negative adsorption state.

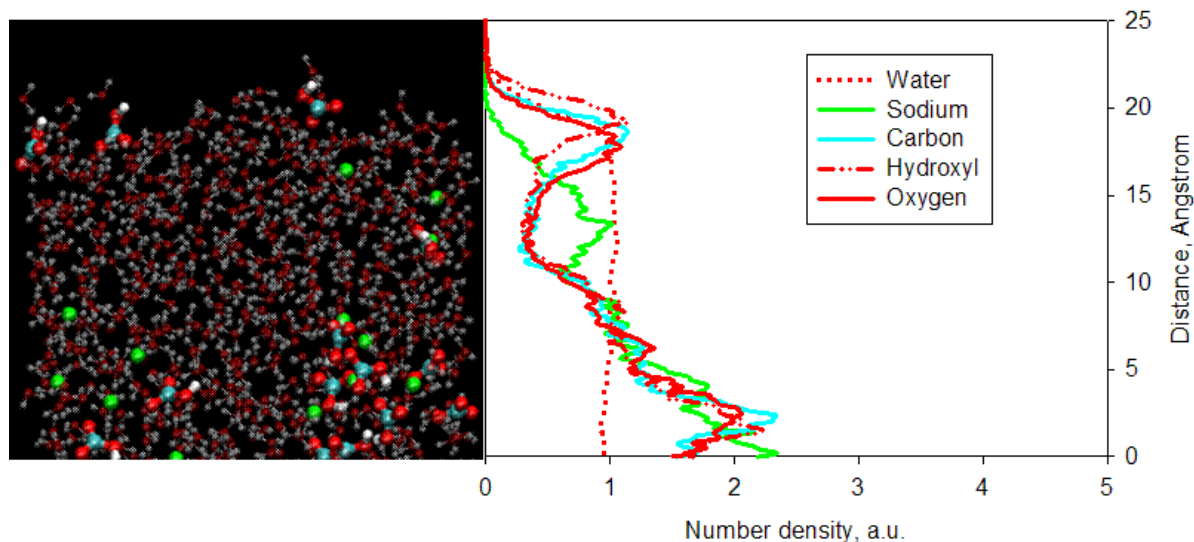


Figure 25. Snapshot of aqueous sodium bicarbonate solution (1.1 M) (left) and particle number density distributions along surface normal (right). The color representations are as follow: Cyan-Carbon, Green-Sodium, Red-Oxygen, and White-Hydrogen (Du et al., 2008).

The changes in surface tension of salt solution (compared to pure water) from MDS analysis and from experimental measurements are listed in Table 3. As seen in Table 3, the calculated surface tension values with respect to the surface tension of pure water are in good agreement with the experimental measurements qualitatively. The significant increase of surface tension of saturated Na_2CO_3 solution is due to the strong negative adsorption of carbonate at the air/water interface as discussed previously; the carbonate ion is excluded from the interfacial region due to strong hydration forces. In contrast, only a slight surface tension increase has been noticed for the saturated NaHCO_3 solution due to a much less significant negative adsorption of the bicarbonate ion at the interface.

Table 3. Comparison of simulated and experimental results for the increase in surface tension relative to pure water (Du et al., 2008)

Salt	Concentration, M	Surface tension change, mN/m	
		MDS calculation	Experimental measurement
Na_2CO_3	2.0	5.6 ± 0.6	3.8
NaHCO_3	1.1	2.0 ± 1.0	0.8

It is also interesting to notice in Figure 26 that the orientations of water molecules in the sodium carbonate solution are totally different when compared to pure water and/or sodium bicarbonate solution as suggested by the sign of $\langle \cos \theta \rangle$. In sodium carbonate solution, the weak local electric field due to the presence of carbonate ions in the middle of the solution has a significant influence on the orientation of water molecules. Thus, the water hydrogen atoms point toward the bulk solution, while the water oxygen atoms point toward the air/solution surfaces. On the other hand, in pure water and sodium bicarbonate solution, the water orientation results from the inhomogeneous properties between the air and the solution phases. Consequently, at the air/sodium bicarbonate solution interface, water hydrogen atoms are in contact with air, and water oxygen atoms are in contact with the aqueous phase.

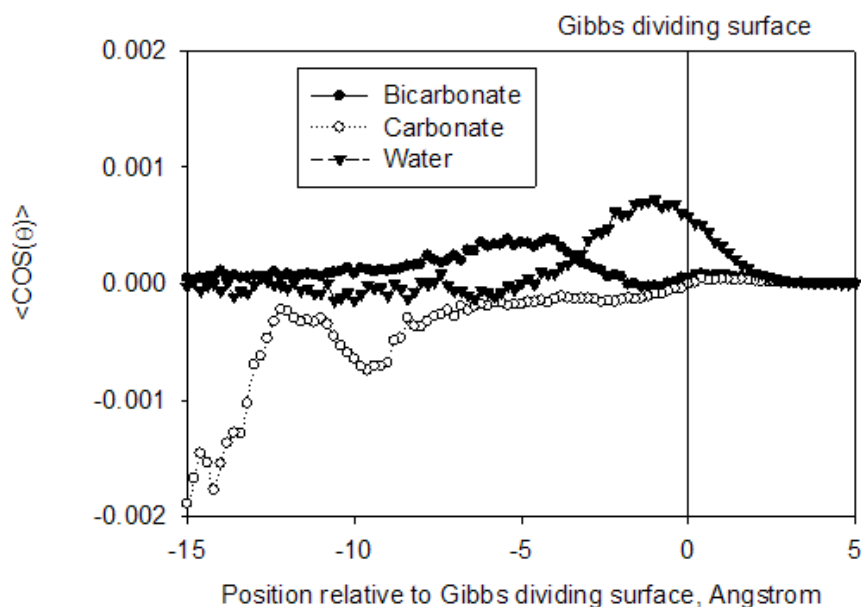


Figure 26. Average water dipole moment $\langle \cos\theta \rangle$ as a function of location in the sodium carbonate, sodium bicarbonate, and pure water solutions from MD simulations. (The Gibbs dividing surface is defined as the position where water density is equal to one-half its bulk density) (Du et al., 2008).

The combination of sum-frequency vibrational spectroscopy (SFVS) and molecular dynamics simulation (MDS) has been validated to be able to provide further information on air/solution interfacial phenomena, especially the interfacial water structures due to the presence of ions (Andersson et al., 2007; Gopalakrishnan et al., 2005; Jungwirth et al., 2006; Jungwirth and Tobias, 2002; Jungwirth and Tobias, 2006; Raymond and Richmond, 2004; Thomas Jennie et al., 2007; Walker and Richmond, 2007a; Walker and Richmond, 2007b). It is reported that charge, size, and polarizability of ions have significant effects on the distribution of ions in the interfacial region (Andersson et al., 2007; Gopalakrishnan et al., 2005; Jungwirth et al., 2006; Jungwirth and Tobias, 2002; Jungwirth and Tobias, 2006; Thomas Jennie et al., 2007). For example, sulfate ions are significantly excluded from the interfacial region (Gopalakrishnan et al., 2005). An increase of water SFVS signal has been obtained due to the substantially expanded interfacial distance and more ordered interfacial water structures due to the strong hydration of the sulfate ions. In addition, calculation of the change of brine solution surface tension from MDS has been reported for selected salts with satisfactory accuracy (Jungwirth and Tobias, 2001; Jungwirth and Tobias, 2006).

4.5 Modelling of adsorption and surface tension of brine solutions

The Gibbs surface thermodynamics has been used to model adsorption at and surface tension of the air-salt solution surfaces. The Gibbs adsorption equation gives the change, $d\sigma$, in surface tension relative to water (solvent) as;

$$d\sigma = -\sum_{i=1}^n \Gamma_i d\mu_i = -kT \sum_{i=1}^n \Gamma_i d \ln(c_i) \quad [1]$$

where Γ_i is the adsorption excess of the i -th solute with the bulk concentration c_i , k is the Boltzmann constant and T is the absolute temperature. The modeling of the adsorption excess is critical to predicting surface tension of salt solutions and has been presented a major modeling challenge for many decades as discussed below.

The increase in surface tension of electrolyte solutions was first modeled by Wagner (Wagner, 1924), and then Onsager and Samaras (Onsager and Samaras, 1934). The potential, E_i , of the repulsive electrostatic image forces on the solute ions was used to determine the adsorption excess by integrating the solute energy from infinity (in solution) to the Gibbs dividing surface as;

$$\Gamma_i = c_i \int_0^{\infty} \left\{ \exp \left[-E_i(x) + z_i e \phi_i \right] / kT - 1 \right\} dx \quad [2]$$

$$E_i(x) = \frac{(z_i e)^2}{4x\epsilon} \frac{\epsilon - 1}{\epsilon + 1} \exp(-2\kappa x) \quad [3]$$

where z_i is the charge of the i -th solute, e is the charge of the proton, κ is the Debye constant, ϵ is the dielectric constant of water, and x is the distance of the i -th solute measured from the Gibbs dividing surface. The electric potential, ϕ_i , of the i -th solute ion was obtained from the solution of the Poisson-Boltzmann equation linearized for the low ionic potential. Onsager and Samaras (Onsager and Samaras, 1934) calculated the surface tension as a sum of a series and tabulated this sum. For very dilute salt solutions, the authors found an analytical expression for the surface tension, referred to as the Onsager-Samaras limiting law nowadays, which shows a linear increase in the surface tension with increasing salt concentration. For 1:1 salts, the limiting law yields

$$\sigma = \sigma_{water} + 1.012c \ln(1.467/c) \quad [4]$$

where the salt concentration is given in M.

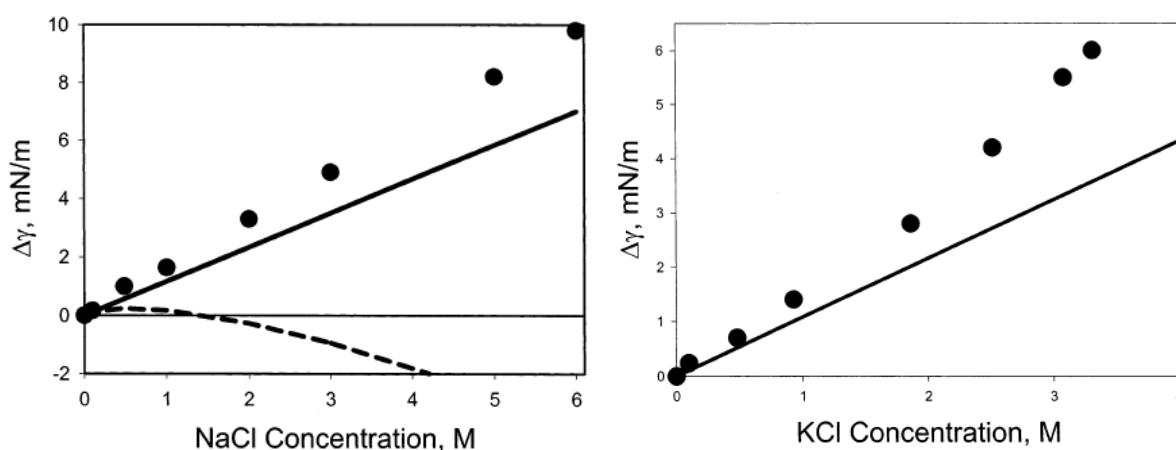


Figure 27. Comparison of the Onsager-Samaras limiting law (dashed line) and the Markin-Volkov theory (solid lines) with the experimental data (points) for the surface tension of sodium and potassium chloride solutions (Markin and Volkov, 2002). $\Delta\gamma = \sigma_{water} - \sigma$.

Further efforts have been focused on developing a theory which accounts for the additional effects on the ion distribution at the surface. Randles considered the effect of ion hydration on the adsorption excess and assumed that there should be an salt ion-depletion layer in the subsurface vicinity (Randles, 1957). The author considered that the smaller ions should have larger hydration radii and vice versa. Therefore, the small ions have a larger affinity to water, resulting in stronger repulsion (expel) from the water-air interface and higher increment of the surface tension as experimentally determined (Weissenborn and Pugh, 1996). The addition of the ion solvation energy into Eq. [2] can improve the prediction of the surface tension of aqueous solutions of inorganic electrolytes (Manciu and Ruckenstein, 2003; Markin and Volkov, 2002). Figure 27 shows a comparison between the experimental data and the theories.

The role of dispersion forces (Mahanty and Ninham, 1977) in the ion-surface interactions has also been investigated (Bostroem et al., 2005; Bostroem and Ninham, 2004; Bostroem et al., 2001; Kunz et al., 2004; Ninham and Yaminsky, 1997). The ion distribution at the surface was obtained by solving the recast Poisson-Boltzmann equation which for 1:1 salts can be described as;

$$\frac{d^2\phi}{dx^2} = -\frac{e[c_+(x) - c_-(x)]}{\epsilon_0\epsilon} \quad [5]$$

$$c_{\pm}(x) = c_0 \exp\left\{-\frac{E_{image} + E_{dispersion} + E_{solvation} \pm e\phi}{kT}\right\} \quad [6]$$

Equations [5] and [6] have to be solved numerically to obtain the ionic potential and the ion distributions which then can be used to calculate the ion adsorption excess and surface tension. Generally, these improved theories show the increase in surface tension of alkali halide solutions. However, the quantitative agreement between the theories and the experimental data is still far from being satisfactory. The magnitude of the surface potential obtained by the theories is also significantly different from the available experimental data.

Molecular dynamics (MD) simulation has also been used to predict the surface tension of alkali halide salt solutions (Jungwirth and Tobias, 2001; Mahiuddin et al., 2008; Minofar et al., 2007). Only qualitative agreement between the MD simulation results and the experimental data has been achieved, i.e., the simulation confirms that the surface tension of alkali halide solutions increases with increasing salt concentration. The simulation also shows different distributions of cations and anions at the air-water surface, i.e., the anions are usually closer to the interface than the cations. Based on these theories, most of the salts increase the surface tension of aqueous solutions which means that salt ions are excluded from the air-brine interface. Our previous studies showed that NaCl and NaF are structure makers. On the contrary, KCl, KI, KNO₃, and K₂SO₄ are structure breaker salts. As seen from the surface tension results of these salts, they increase the surface tension of aqueous solutions.

It is noted that, while the molecular modeling of the adsorption excess of salt ions and the surface tension of salt solutions has been difficult, a semi-analytical approach to the prediction of the surface tension can be useful. It is based on the Gibbs adsorption equation and the empirical correlation of the ion activity with the salt concentration (Ozdemir et al., 2006; Ozdemir et al., 2009b). The Gibbs adsorption equation used in this modeling exercise is generally expressed in term of the ion activity, a , rather than the concentration used in Eq. [1] which is normally correct for low concentration only. For cation, M, and anion, X, dissociated from a single salt, MX, the Gibbs adsorption equation used is given as;

$$d\sigma = -kT \left[v_X \Gamma_X d(\ln a_X) + v_M \Gamma_M d(\ln a_M) \right] \quad [7]$$

where v_M and v_X are the stoichiometric coefficients of the salt. Equation [7] can be used, in conjunction with the Langmuir adsorption isotherm for the salt ions and the Pitzer theory (Pitzer, 1973; Pitzer and Kim, 1974; Pitzer and Mayorga, 1973; Pitzer and Mayorga, 1974) for the ion activities, a_{\pm} , to calculate the surface tension as a function of salt concentration.

Figure 28 shows a few examples of the model predictions for the surface tension of sodium and potassium chloride, and sodium carbonate and bicarbonate with concentration up to the limit of saturation. The agreement is excellent. The only disadvantage of the semi-empirical modeling approach is the required dependence of the ion activity on the salt concentration. However, for many typical salts, the dependence is already measured and readily available.

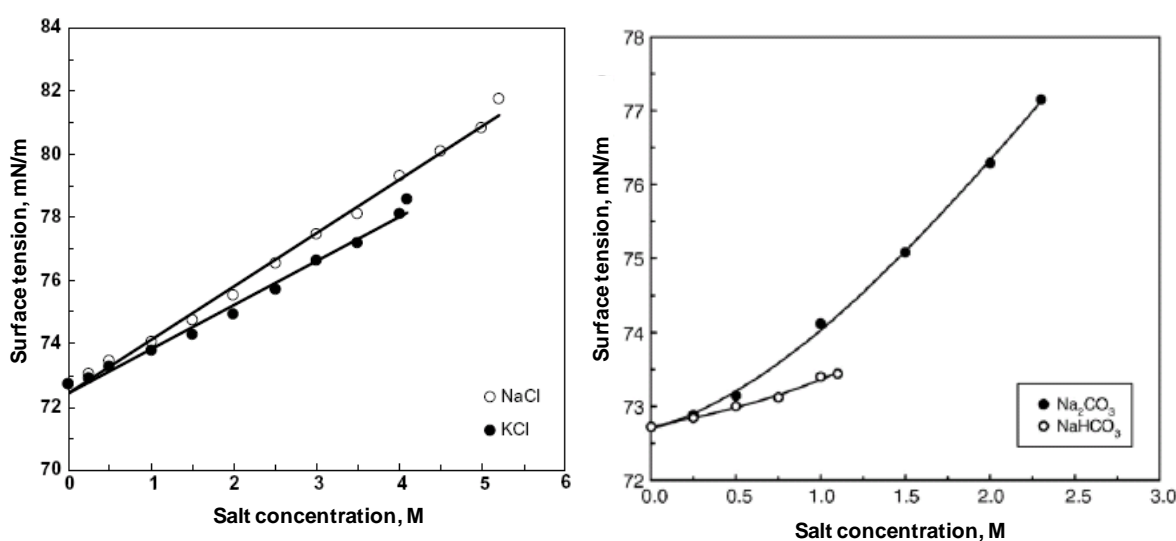


Figure 28. Comparison between the surface tension data (points) and the semi-empirical predictions (lines) based on Eq. [7], the Langmuir adsorption isotherm and the the Pitzer theory for the ion activity (Ozdemir et al., 2006; Ozdemir et al., 2009b).

5. Effect of ions at the solid/brine interfacial properties

5.1 Contact angle

Contact angle measurements are often used in flotation studies to describe the extent of wetting or the hydrophobicity of a surface. It appears from previous studies that in the presence of water structure maker ions, salt surfaces are hydrated to the greatest extent, and a contact angle is not detected, whereas in the presence of water structure breaker ions the surface appears to be less hydrated and finite contact angles can be measured in the absence of collector (Hancer et al., 2001). For example, Table 4 presents sessile drop contact angle measurements with a drop of brine in the absence of collector (Hancer et al., 2001).

Table 4. Advancing contact angle on soluble salt crystals in their saturated solutions in the absence of collectors (Ozdemir et al., 2009a)

Salt	Contact Angle, degree
------	-----------------------

KI	25±2
KCl	7.9±0.5 (12±1.4)
NaCl	0
NaF	0
Na ₂ CO ₃	0
NaHCO ₃	19.8
Trona	0.4

The contact angle measured for carbonate salts using the thin-layer wicking method also indicated that the surfaces of structure making salts such as Na₂CO₃ and trona were hydrated to such a great extent that a contact angle could not be measured for these salts, whereas the structure breaking NaHCO₃ salt was less hydrated and a finite contact angle was measured.

Table 5. Bubble attachment results for selected alkali salts (Yalamanchili et al., 1993)

Alkali halide	Bubble Attachment
LiF	N
NaF	N
KF	N
RbF	N
CsF	N
LiCl	Y
NaCl	N
KCl	Y
RbCl	N
CsCl	Y
LiBr	Y
NaBr	Y
KBr	Y
RbBr	Y
CsBr	Y
LiI	Y
NaI	Y
KI	Some
RbI	Y
CsI	N
NaI.H ₂ O	N

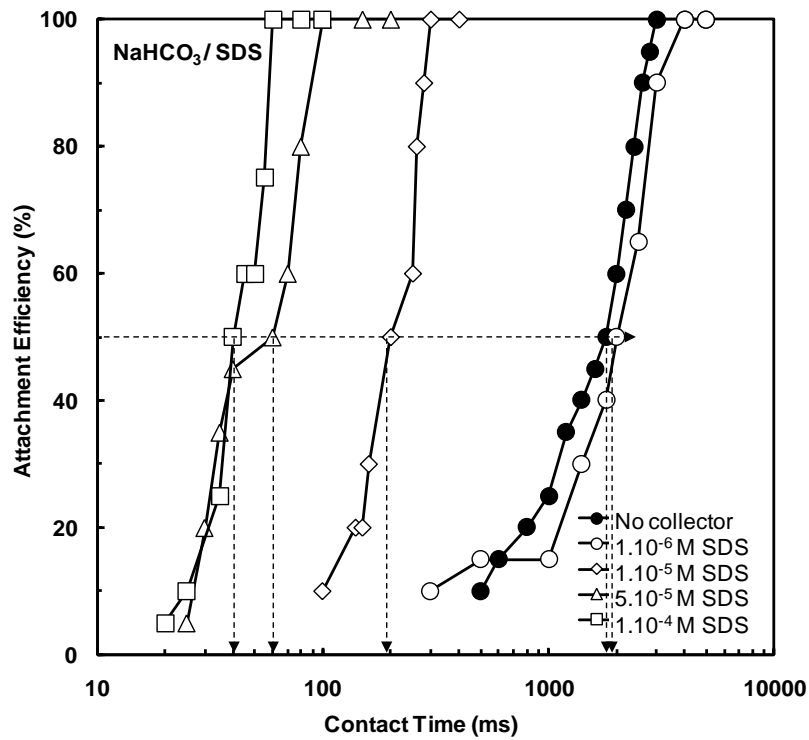
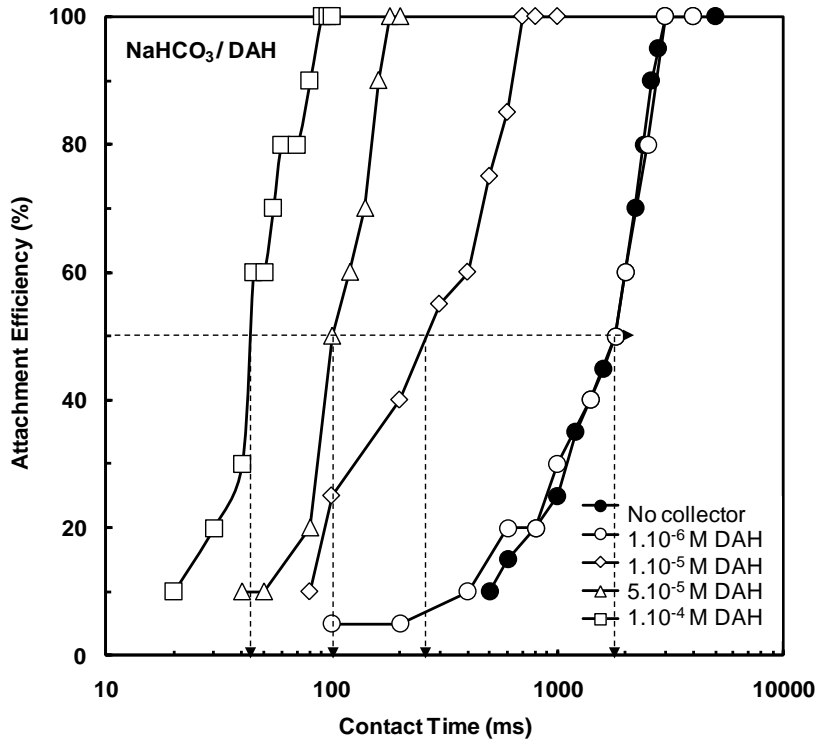


Figure 29. The effect of (top) DAH and (bottom) SDS concentration on attachment time between air bubbles and NaHCO₃ particles at pH 8.4 in saturated solution of NaHCO₃ (1.1 M) (Ozdemir et al., 2009a).

Table 6. Measured attachment times for different concentrations of DAH and SDS at a bed of NaHCO_3 and Na_2CO_3 particles (150×106 microns) (Ozdemir et al., 2009a)

Collector Concentration (M)	Attachment time with NaHCO_3 (ms)		Attachment time with Na_2CO_3 (ms)	
	DAH	SDS	DAH	SDS
No collector	1800	1800	No attachment	No attachment
1×10^{-6}	1800	1800	No attachment	No attachment
1×10^{-5}	270	200	No attachment	No attachment
5×10^{-5}	100	60	NA	NA
1×10^{-4}	45	40	No attachment	No attachment

5.2 Bubble attachment time

The bubble attachment time experiments can also be carried out to characterise the hydrophobicity of mineral particles either in their natural state or with surfactant addition. Table 5 presents the bubble attachment results for selected alkali salts with dodecylamine hydrochloride. As seen from the table, while there is an attachment between the structure breaker salts such as KCl, CsCl, and RbBr etc., and bubble, no attachment was observed between the structure maker salts such as NaCl, and RbF and KF etc, and bubble (Yalamanchili et al., 1993).

Ozdemir et al (Ozdemir et al., 2009a) studied the bubble-particle attachment carbonate and bicarbonate soluble salts with dodecylamine hydrochloride and sodium dodecyl sulphate in detail. As seen in Figure 29, there is an attachment between the NaHCO_3 particles and a bubble, and the bubble attachment times for NaHCO_3 decrease with increasing DAH and SDS concentrations. However, in the case of Na_2CO_3 , as seen from Table 6, there is no attachment of Na_2CO_3 particles in its saturated solutions (2.3 M) even at high concentrations of DAH and SDS.

The results shown in Table 6 indicated that NaHCO_3 surface has a lower stability which allows easier penetration of both anionic and cationic collectors to the surface of NaHCO_3 leading to good flotation, as shown in bubble attachment time measurements. However, it is not the case for Na_2CO_3 . This can be explained by the fact that the ion specific effect plays an important role on attachment time of these salts. For instance, dissolved ions Na^+ and CO_3^{2-} can significantly affect the interfacial water structure at the salt surface and inhibits the bubble-particle attachment which accounts for the difficulty in the flotation of Na_2CO_3 . In contrast, the Na^+ and HCO_3^- ions cause only a modest increase in water structure at the salt surface and make the bubble-particle attachment possible which accounts for the flotation of NaHCO_3 .

5.3 Electrokinetics of soluble salt minerals

Sparingly soluble minerals when dissolved in water will release a number of species into solution. These ionic species will be produced at the solid-liquid interface or may form in solution and subsequently adsorb on the solid in amounts proportional to their concentrations. The electrokinetic behavior is an indicator of the ability of ions to be incorporated in the double layer and, in particular, may reveal the expected flotation response for a certain collector scheme. In this matter, the measurement of surface charge is always important to understand the interaction between mineral and collector. The electrophoretic mobilities, surface charge and floatability of the salt crystals are presented in Table 7. As seen from the table, even the negatively charged salts can float with both the cationic (DAH) and anionic (SDS) collectors,

whereas the others are not floated with either of collector. It is clear from these results that surface charge is not a particularly important factor in the flotation of the salts (Veeramasuneni et al., 1997; Yalamanchili et al., 1993).

Table 7. Electrokinetic mobility, surface charge and floatability of some salt crystals (Hancer et al., 2001; Ozdemir et al., 2009a)

Salt	Electrophoretic Mobility (ζ /sec)/(V/cm)	Surface Charge	Flotation	
			DAH	SDS
KCl	-0.43±0.19	-	Yes	Yes
NaCl	+0.19±0.10	+	No	No
NaF	+0.16±0.12	+	No	No
Na ₂ B ₄ O ₇ ·10H ₂ O	-1.68±0.11	-	Yes	Yes
Na ₂ CO ₃	-0.91±0.23	-	No	No
NaHCO ₃	-1.16±0.31	-	Yes	Yes

As mentioned before, boron minerals exhibit a spectrum of different chemical compositions with cations ranging from monovalent to multivalent ions. The type and valency of the cation dictate the solubility of the mineral and in turn its electrokinetic behavior. Salt type minerals such as borates release a number of species upon dissolving in water. For example, colemanite containing Ca²⁺ ion in its structure undergoes acid base reactions in the vicinity of pH 9.3. The following overall dissolution process for colemanite occurs in a system open to the atmosphere (Celik and Yasar, 1995). As seen from Figure 30, the iep of borax appears to be absent or impossible within the pH range of stability. Further studies showed that the potential determining ions (pdi) for borax are found to be the constituent lattice cations, i.e., the anion B₄O₇²⁻ (borate), and the H⁺ and OH⁻ ions which control ratio of HCO₃⁻/CO₃²⁻ (Celik and Yasar, 1995; Yasar, 1985).

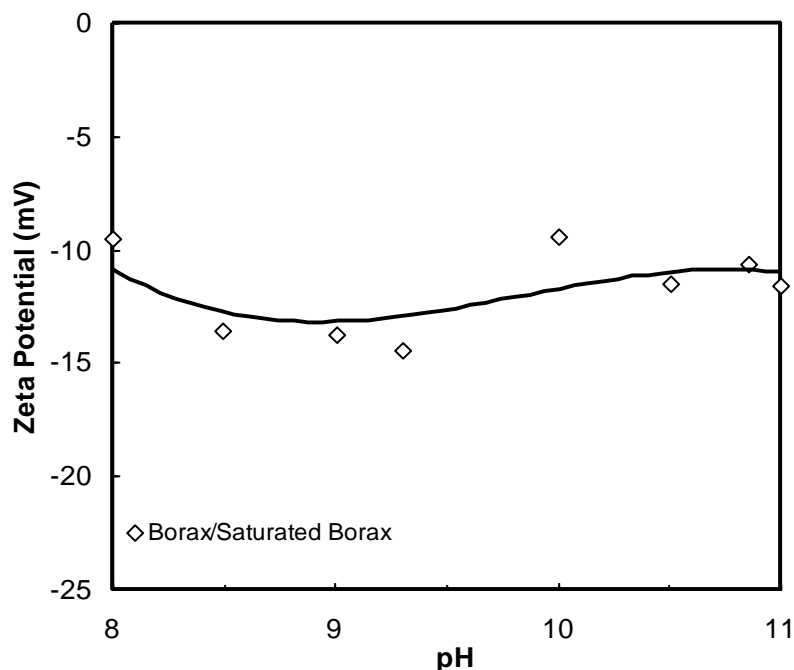


Figure 30. Zeta potential of borax as a function of pH (Muduroglu et al., 2000).

Zeta potential measurements of borax were further conducted with SDS and DAH collectors in order to test the validity of electrostatic interactions in saturated borax solutions. Figure 31 presents the zeta potential profiles of borax in the presence of SDS and DAH. While DAH reduces the zeta potentials from -14.4 down to -1.6 mV, SDS increases the negative charges from -14.4 up to -26.1; these results distinctly illustrate the existence of electrostatic interactions in the system.

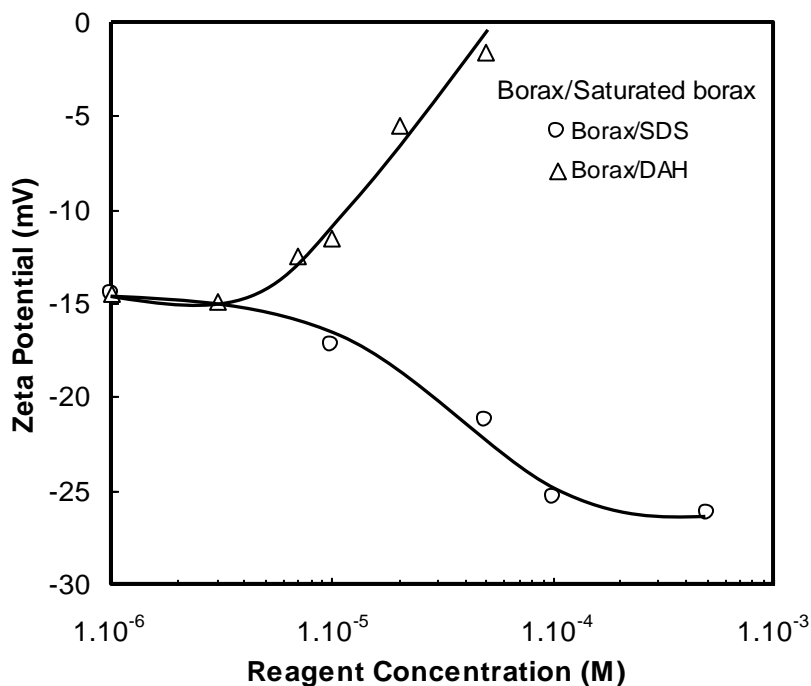


Figure 31. Zeta potential of borax in the presence of anionic (SDS) and cationic (DAH) collectors (Muduroglu et al., 2000).

5.4 Molecular dynamics simulations

The obvious change of water molecule orientations at different alkali chloride crystal surfaces is due to the variation of cation size and consequently the coulombic interaction between water molecules and lattice ions at salt surface. When small Li^+ ions are present, the interaction between surface Li^+ ions and the oxygen atoms of water molecules dominates compared to the interaction of water hydrogen and surface Cl^- ions due to the larger local electric field around the small Li^+ (Koneshan et al., 1998b). Therefore, at a LiCl crystal surface, a layer of water molecules with oxygen atoms in close contact at the crystal surface and hydrogen atoms stretched out to the water phase (represented schematically in Figure 32a) is energetically favorable. The presence of the second water layer with opposite orientation neutralizes the dipole moment of water molecules in the first layer. As the cation size increases, the magnitude of local electric field decreases accordingly, thus, at a NaCl surface water molecules tilt to such an orientation that water oxygen atoms are further away from the crystal surface while water hydrogen atoms are closer to the surface as seen in Figure 32b. Similar water structures at a NaCl crystal surface have also been obtained from ab initio calculation (Pramanik et al., 2005), density function calculation (Park et al., 2004), and Monte Carlo simulations (Engkvist and Stone, 2000). With further increase of cation size to K^+ and Rb^+ , the interaction between water hydrogen atoms and surface Cl^- ions is significant enough

to compete with the cation/water oxygen interaction. Hence a hydrogen/oxygen/hydrogen configuration of interfacial water molecules seen in Figure 32c is favored.

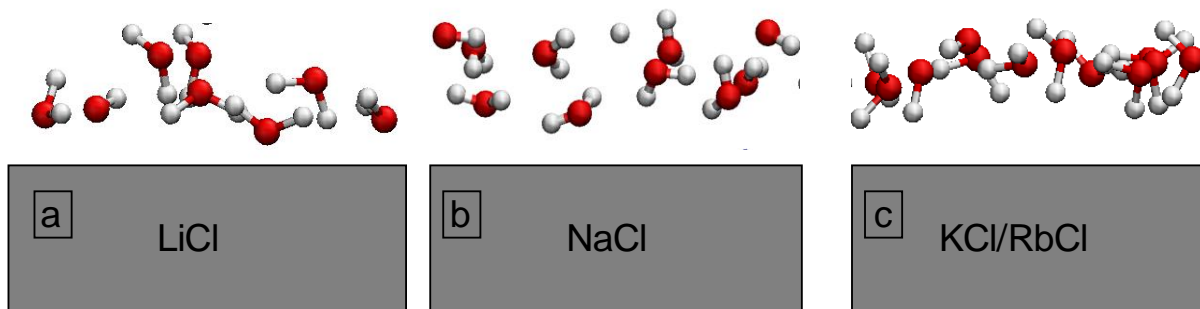


Figure 32. Schematic representations (from simulation snapshots) describing different orientation of interfacial water molecules at different alkali chloride surfaces (Du and Miller, 2007b).

The interfacial water structure at different alkali halide salt surfaces can be further studied from the water dipole moment distributions at the crystal surface. Figure 32 describes the water dipole moment density distribution profiles along crystal surface normal for LiCl and KCl respectively. It is observed in Figure 33a for the LiCl surface that a sharp peak for α is found at around 20° followed by another major peak for α at around 120° . With further increase in the cations size, some dramatic changes are observed as illustrated in Figure 33b for the KCl system. The two interfacial water layers at LiCl crystal surface have been replaced by one layer with two density peaks for α located at around 130° and 40° , respectively, and the magnitude of the peak is slightly larger at 40° . The orientation of interfacial water molecules at the KCl crystal surface is a result of the balance between K^+ ion/oxygen and Cl^- ion/hydrogen interactions, and suggests that these two interactions are of comparable magnitude. The water molecules show significant disorder.

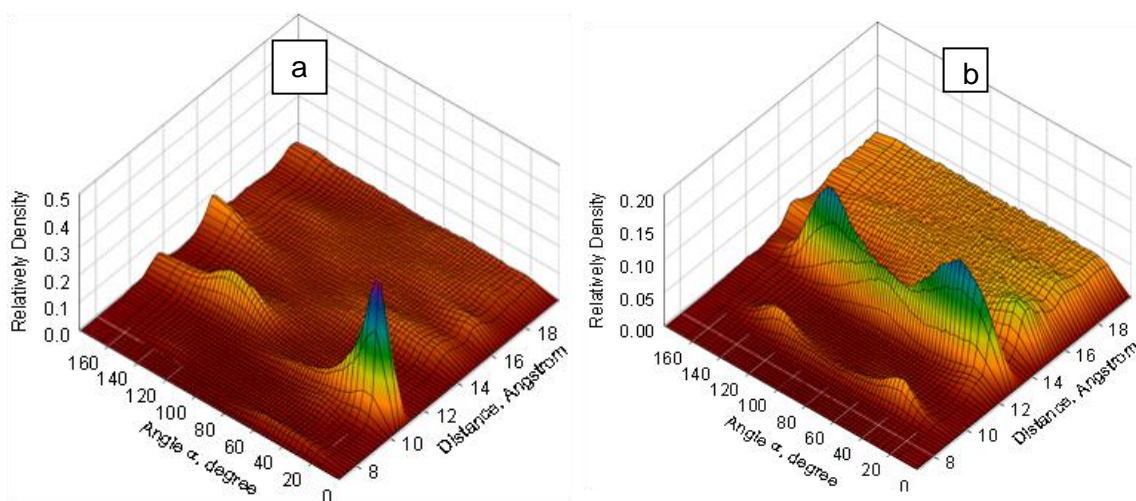


Figure 33. Water dipole moment (angle α) density distribution LiCl and KCl salt surface normal (Du and Miller, 2007b).

An accurate measurement of equilibrium alkali halide crystal surface charge has always been a challenging task due to the dynamic dissolution and recrystallization processes which happen at the crystal surface. The surface charge of alkali halide crystals in saturated solution has been calculated as the summation of cation and anion number density at a designated distance from the surface, and the sign of the salt surface charge is summarized in Table 8. For comparison, theoretical and experimental results reported in the literature are listed as well.

Table 8. Surface charge of selected alkali halide crystals in saturated solution and comparison with analytical model and experimental results (Du and Miller, 2007b)

Salt	Cutoff Distance (Angstrom)	Surface Charge		
		This Study (MDS)	Analytical Model (Veeramasuneni et al., 1997)	Experimental Results (Miller et al., 1992; Yalamanchili et al., 1993)
LiCl	12.5	-	-	-
NaCl	13.0	+	+	+
KCl	14.0	+	+	-
RbCl	14.0	+	+	+

The sign of the surface charge for selected alkali chloride salt surfaces in saturated solutions obtained from this MD simulation study are in excellent agreement with the results from extended lattice hydration theory results, which takes into consideration the lattice ion hydration free energy as well as ion size effects (Veeramasuneni et al., 1997). It has been suggested that surface lattice ions are partially hydrated; therefore, instead of considering ion hydration energy alone, which accounts for the hydration of the gaseous ions, an ion-water dipole interaction has to be considered (Veeramasuneni et al., 1997). This ion-water dipole interaction accounts for the transaction of a partially hydrated surface lattice ion to be a free (vacuum) surface lattice ion (Veeramasuneni et al., 1997). In LiCl system, due to a much larger hydration energy (-470.7 kJ/mole for Li^+ and -347.27 kJ/mole for Cl^- (Hunt, 1963; Miller et al., 1992), Li^+ ions in the LiCl crystal lattice have a greater tendency than Cl^- ions to be dissolved into water, therefore leaving the salt surface negatively charged (Miller et al., 1992; Veeramasuneni et al., 1997; Yalamanchili et al., 1993). In contrast, due to a much larger ion-water dipole interaction (-35.37 kJ/mole for Cl^- and 4.3 kJ/mole for Na^+ (Veeramasuneni et al., 1997), the dissolving of partially hydrated surface lattice Cl^- is energetically more favorable than the dissolving of surface Na^+ despite the fact that Na^+ has a larger hydration energy (-371.54 kJ/mole) (Hunt, 1963; Veeramasuneni et al., 1997). For KCl and RbCl salts, the hydration of Cl^- is dominating, consequently, the salt surfaces are positively charged (Veeramasuneni et al., 1997). The obvious difference with respect to the sign of the surface charge for the KCl experimental results has been attributed to the presence of oxygen defects in the KCl crystal lattice (Veeramasuneni et al., 1997; Yalamanchili et al., 1993). Also, from the extended lattice hydration theory, the difference between hydration energies of K^+ and Cl^- is 3.46 kJ/mol (Veeramasuneni et al., 1997; Yalamanchili et al., 1993), and this might account for the anomalous behavior of KCl during the sensitive nonequilibrium electrophoresis measurement (Veeramasuneni et al., 1997; Yalamanchili et al., 1993). The consistency between MD simulation and the literature results regarding the surface charge of alkali halide salt crystal suggests that the MD simulation provides a valid method for the analysis of surface charge in the case of ionic solids.

The dynamics of water molecules at selected alkali chloride salt surface study has concluded that first of all, in general, water molecules in KCl and RbCl saturated solutions diffuse significantly faster than they do in NaCl and LiCl saturated solution. This is because in

NaCl and LiCl solutions the cation/water interaction is stronger, and thus water molecules have been immobilized to a greater extent. Similar observations have also been reported for a variety of alkali halide solutions (Allen and Tildesley, 1987; Chowdhuri and Chandra, 2001; Du and Miller, 2007b; Du et al., 2007a; Koneshan and Rasaiah, 2000; Koneshan et al., 1998b). Secondly, the self-diffusion coefficient for water molecules in the salt/water interfacial region is significantly lower than that of in bulk water. In the interfacial region, where ion dissolution/deposition processes dominate, there is a substantial accumulation of ions. As a result, the movement of water molecules in this region is confined due to the ion/water interactions. Thirdly, the diffusion of water molecules in bulk shows strong concentration dependence. In LiCl saturated solution (~14 M), the self-diffusion coefficient of water molecules in the bulk solution ($\sim 0.8 \cdot 10^{-9} \text{ m}^2/\text{sec}$) is significantly lower than the self-diffusion coefficient in pure water ($\sim 2.5 \cdot 10^{-9} \text{ m}^2/\text{sec}$) (Berendsen et al., 1987; Du and Miller, 2007b; Du et al., 2007a) due to the large concentration of ions (especially Li^+ ions) which interact strongly with water molecules and immobilize them. In contrast, in KCl saturated solution (~4.8 M), the water self-diffusion coefficient in bulk solution ($\sim 2.5 \cdot 10^{-9} \text{ m}^2/\text{sec}$) is similar to the value of pure water. Possible explanation is that a large number of ions are accumulated in the crystal/water interfacial region, thus ion concentration in bulk solution is relatively low. Also, the ion/water interactions are weaker when compared to LiCl system, and consequently water molecules are more mobile.

For water molecules in the interfacial region, their residence time shows clear cation dependence as $\tau_{\text{LiCl}} > \tau_{\text{NaCl}} > \tau_{\text{KCl}} \approx \tau_{\text{RbCl}}$. This is due to the fact that small cations such as Li^+ and Na^+ interact stronger with water molecules when compared to large cations such as K^+ and Rb^+ , consequently, water molecules are immobilized more significantly around small cations. The inconsistency involving KCl and RbCl interfacial water is due to a higher RbCl saturation solution concentration. The variation of interfacial water residence time is in excellent agreement with water self-diffusion coefficients. In bulk solutions, water molecules move faster when compared to water molecules at crystal lattice positions and interfacial water molecules as indicated by the short residence times and large diffusion coefficients. Especially for water molecules in bulk KCl solution, the residence time (5.9 ps) and self-diffusion coefficient ($\sim 2.5 \cdot 10^{-9} \text{ m}^2/\text{sec}$) are very close to pure water value ($\sim 5 \text{ ps}$ and $\sim 2.5 \cdot 10^{-9} \text{ m}^2/\text{sec}$ respectively) (Berendsen et al., 1987; Du and Miller, 2007b; Du et al., 2007a; Koneshan et al., 1998b).

5.5 General discussion

A high concentration of dissolved ions in brines modifies the bulk and interfacial water structure, and this effect is a significant factor in the flotation chemistry of soluble salts. Particularly, recent studies showed that consideration of hydration phenomena at salt crystal surfaces provides a better explanation for the flotation of soluble salts even when the collector is charged the same as the salt and the flotation of soluble salts depends on the dissolved ions of these salts (Du et al., 2008; Hancer et al., 2001; Miller et al., 1992; Ozdemir et al., 2007; Ozdemir et al., 2009a; Ozdemir et al., 2006). The previous studies in dilute electrolyte solutions also showed the same effect of structure making and breaking properties of salt ions on the adsorption process (Ma and Pawlik, 2006).

All the results show that the dissolved ions significantly affect the flotation of these soluble salts. While some dissolved ions activate the flotation of minerals, some of them reduce the flotation of these salts. As mentioned before while NaHCO_3 floats with both anionic and cationic collectors, Na_2CO_3 does not float at all. It can be said that NaHCO_3 surface has a lower stability which allows easier penetration of both anionic and cationic collectors to the surface of NaHCO_3 leading to good flotation as shown in bubble attachment

time measurements. However, this is not the case for Na_2CO_3 . This can be explained by the fact that the ion specific effect plays an important role on the bubble attachment time at the surface of these salts. For instance, dissolved ions Na^+ and CO_3^{2-} can significantly affect the interfacial water structure at the salt surface and inhibit the bubble-particle attachment which accounts for the difficulty in the flotation of Na_2CO_3 . In contrast, the Na^+ and HCO_3^- ions cause only a modest increase in water structure at the salt surface and make the bubble-particle attachment possible which accounts for the flotation of NaHCO_3 .

Trona does not float well in its saturated brine with DAH (Ozdemir et al., 2009a). Additionally, the limited floatability of trona with DAH is reduced slightly after adding 1×10^{-2} M of Na_2CO_3 to the brine. This result indicates that the structure making character of Na_2CO_3 has a significant impact on trona flotation, making the direct flotation of trona from its brine difficult. The same effect was also observed in the flotation of NaHCO_3 in the presence of Na_2CO_3 . These results suggest that the effect of the bicarbonate ion on the water structure is negligible when compared to the carbonate ion. It appears from these results that when one of the ions in a salt is a water structure breaker whereas the other a structure maker, one of them might be dominant in determining the extent of water structuring. The results reported here indicate that instead of Na^+ ion, which is normally a structure maker, it is rather the HCO_3^- anion, a structure breaker, dominates water structuring in soluble salt systems. All this discussion refers to water structure making and braking effect of ions. However, MDS studies are not conclusive in this. Ion specificity appears to be significant. Thus the above analysis on trona does not include this aspect.

6. Conclusions

The flotation chemistry of soluble salts such as alkali halides and alkali oxyanion salts has been studied by many researchers and it appears that the interfacial water structure and hydration states of soluble salt surfaces are of considerable importance in explaining their flotation behavior. Generally, soluble salts can be classified as structure makers or as structure breakers. Structure making salts such as NaCl , strongly bond/order water molecules at the salt surface, prevent adsorption of collector, and inhibit flotation with either a cationic or an anionic collector. Structure breaking salts such as KCl have a tendency to disorganize the structure of water at the salt surface; thus a collector may more easily reach the surface, creating the hydrophobic state and further allowing for the flotation of such structure breaking salts with both cationic and anionic collectors.

The flotation behaviour of soluble salt minerals is influenced by dissolved salts and is determined by the specific effect of these ions. The effect of these ions at air/liquid, air/solid, and solid/liquid interfaces has been investigated in more detail using several experimental techniques. All of these studies suggest that ion specificity is the most significant factor in governing the flotation surface chemistry of soluble salt minerals with both anionic and cationic collectors.

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