INVITED FEATURE

Flotation chemistry of soluble salt minerals: from ion hydration to colloid adsorption

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Abstract

In this paper, recent progress with respect to the flotation chemistry of soluble salt minerals is reviewed, and some of the more relevant issues including the hydration states of ions, the interfacial phenomena of salt surfaces and the flotation behavior of selected soluble salts are discussed. Due to the high solubility, the flotation of most soluble salts has to be carried out in their saturated brines. Anecdotal evidence has suggested that the hydration states of the ions have significant influence on the physicochemical properties of the solutions, the surface charge and wetting characteristics of the minerals, the collector adsorption states and, further, the flotation behavior of the soluble salts. In this regard, reviewing past research findings, efforts are made to establish a correlation between the ion hydration states with the flotation behavior of the soluble salts. Further, advances in understanding the significance of colloid adsorption involved in the soluble salt flotation process are addressed, and future research efforts to understand the soluble salt flotation chemistry are suggested.

Introduction

Soluble salt minerals are essential raw materials for the production of a variety of commodities, fertilizers, potassium hydroxide, soda ash, magnesium com- pounds and other chemicals. These soluble mineral resources can be processed using flotation technology and, currently, more than 80% percent of the world's potash is produced by the selective flotation of KCl crystals (sylvite) from other salt

crystals, predominately NaCl (halite) and other more complex salts (Searls, 1990). Despite the successful application of flotation technology in the potash industry, the mechanisms for collector adsorption on soluble salts have not yet been fully understood and, therefore, have been of considerable interest to flotation researchers for many decades.

In 1933, Halbich proposed that the flotation of halite from sylvite with carboxylic acid is due to the preferential formation of sodium carboxylates, which are less soluble than potassium carboxylates (Halbich, 1933). Later investigation by Singewald (Singewald, 1961; Searls, 1990) and other researchers (Roman et al., 1968) using anionic collectors proved the inadequacy of Halbich's insoluble collector compounds theory.

The ion substitution theory is probably the simplest theory for collector adsorption. This theory states that the selective adsorption of an amine collector at the KCl surface is a result of the replacement of surface lattice K^+ ions with RNH_3^+ ions. In contrast, RNH_3^+ ions cannot fit in the NaCl crystal due to the size of Na^+, which is smaller than the RNH_3^+ ion head group. This theory was extended to all alkali salts by D.W. and M.C. Fuerstenau in 1956 (Fuerstenau and Fuerstenau, 1956). According to their study, only those minerals with a surface cation size similar to the RNH_3^+ ion can be floated. This theory does not provide satisfactory explanation for the flotation response with carboxylate, sulfate and sulfonate collectors (Singewald, 1961; Roman et al., 1968; Searls, 1990).

The surface charge theory was proposed by Roman et al. (1968). The collector adsorption was related to the expected sign of the surface charge of salt minerals. Later research efforts by Miller et al. demonstrated that KCl particles are negatively charged and NaCl particles are positively charged (Miller et al., 1992; Yalamanchili et al., 1993). Thus, it has been proposed that collector adsorption originates from the heterocoagulation between oppositely charged collector colloids and soluble salt mineral particles, and this theory explains the amine flotation separation of KCl from NaCl. However, the effective flotation behavior of negatively charged KCl with the anionic collector sodium dodecyl sulfate (SDS) (Rogers and Schulman, 1957; Schubert, 1988; Searls, 1990) is not in accord with this explanation.

Rogers and Schulman (Rogers, 1957; Rogers and Schulman, 1957) studied the hydration of salt surfaces and collectors in the 1950s, and they proposed that collector adsorption could be explained in terms of the competition between the collector molecules and water molecules at the salt surface. This hydration theory stated that weakly hydrated salt minerals such as KCl can be floated by alkyl amines and alkyl sulfates, which do not hydrate in aqueous solution. In contrast, strongly hydrated salt minerals such as NaCl can be floated by fatty acids, which can hydrogen bond with the salt surfaces. For excessively hydrated salt minerals, no collector adsorption occurs and, consequently, flotation cannot be achieved. Unfortunately, no solid evidence has been provided to support such a position.

Subsequent study of water structures in alkali halide solutions by Miller et al. indicated that interfacial water structure may play a more significant role regarding collector adsorption on alkali halide salts (Hancer and Miller, 2000; Hancer et al., 2001; Du and Miller, 2007; Cao et al., 2010; Ozdemir et al., 2010; Cao et al., 2011; Ozdemir et al., 2011). The alkali halides are conveniently categorized as either water "structure makers" (salts which facilitate the intermolecular hydrogen bonding between water molecules) or water "structure breakers" (salts which disrupt the hydrogen bonding between water molecules), depending on their affinity to water molecules. For structure-breaking salts such as KCl, both anionic and cationic

surfactants appear to adsorb at the salt particle surface by replacing interfacial water molecules (Hancer et al., 2001; Cao et al., 2010; Ozdemir et al., 2011). In contrast, no collector adsorption occurs at structure-making salt surfaces such as NaCl due to the strong ion/water interactions (Hancer et al., 2001). This theory has successfully explained the selective flotation of KCl from NaCl with alkyl amines and alkyl sulfates as collectors; however, this theory appears to be inadequate to explain the flotation behavior of NaCl using alkyl morpholine (Titkov, 2004) and alkyl carboxylate as collectors (Miller et al., 1992).

Analysis of soluble salt flotation is further complicated by the fact that, instead of diffusion and selective adsorption of dissolved collector molecules at the mineral surface, which occurs in many flotation systems, the flotation of KCl from NaCl with alkyl amines and alkyl sulfates seems to be possible when the solubility limit of the collectors is exceeded (Leja and Schulman, 1954; Rogers and Schulman, 1957; Roman et al., 1968; Schubert, 1988; Searls, 1990; Miller and Yalamanchili, 1994; Miller et al., 1997; Laskowski et al., 2007; Schreithofer and Laskowski, 2007; Burdukova et al., 2009), suggesting that the adsorption of collector colloid may be involved (Hancer et al., 2001; Schreithofer and Laskowski, 2007; Burdukova et al., 2009). However, the flotation of alkali oxyanion salts (K_2SO_4 for example), which occurs at collector concentrations below the solubility limit, does not fully confirm this mechanism (Hancer et al., 2001).

In view of the above, it is worth noting that the established theories have yet to provide a satisfactory explanation with respect to the soluble salt flotation chemistry and, as pointed out by Leja (Leja and Schulman, 1954; Leja, 1983), factors including crystal lattice, ionic size, hydration of polar groups and salt surfaces, solubility of surfactants and their complexes, surface charge, temperature, etc. all could contribute to the flotation chemistry. In addition, there are physical parameters due to hydrodynamics, agitation, etc. Each parameter, whether physical or chemical, becomes of critical importance in a particular set of conditions, but otherwise may not play any major role (Leja and Schulman, 1954; Leja, 1983). The lack of consistency of the above mentioned theories in explaining the different soluble salt flotation behaviors is mainly attributed to the experimental difficulties in obtaining direct evidence to understand the interfacial phenomena and adsorption states. Such experimental difficulties originate from the unique features of soluble salt flotation practice, which occur in saturated brines. Some of the distinct features are summarized below:

- Strong hydration of ions.
- Instability of mineral surface in high viscosity medium.
- Complete compression of electrical double layer.
- Significant collector salting out effect.

In this regard, the purpose of this paper is to review the recent progress made in understanding soluble salt flotation chemistry, and some of the critical issues including ion hydration and mineral surface hydration states, as well as collector adsorption mechanisms, will be discussed to provide information for future research efforts.

Brines and ion hydration

Unlike other mineral flotation processes, the flotation of soluble salts has to be performed in their saturated brines to prevent the constant dissolution of salt crystals. Due to the high solubility of most soluble salts, when the solution is saturated with ions, hydrated more or less with surrounding water molecules, some of the physicochemical properties of

Table 1 — Solubility and hydration number of alkali halide solutions at 25° C (solubility data are obtained or taken from Nickolov and Miller (2005) and hydration number data are obtained or taken from Koneshan et al. (1998b) Varma and Rempe (2006) and Du and Miller (2007)).

Salt	Solubility, g/100 g water 25° C	Water-to-ion ratio	Cation hydration number	Anion hydration number	Total hydration number
NaF	4	29.2	5-6	6-7	11-13
KF	92	1.8	6-7	6-7	12-14
RbF	300	2.2	6-8	6-7	12-15
CsF	367	1.2	7-8	6-7	13-15
LiCl	85	2.1	4-5	6-8	10-13
NaCl	35.9	4.5	5-6	6-8	11-14
KCl	34.4	6.0	6-7	6-8	12-15
RbCl	91	3.7	6-8	6-8	12-16
CsCl	186	2.5	7-8	6-8	13-16
LiBr	167	1.4	4-5	6-8	10-13
NaBr	91	3.1	5-6	6-8	11-14
KBr	68	4.9	6-7	6-8	12-15
RbBr	110	4.7	6-8	6-8	12-16
CsBr	124	4.8	7-8	6-8	13-16
LiI	151	2.5	4-5	7-8	11-13
NaI	184	2.3	5-6	7-8	12-14
KI	140	3.3	6-7	7-8	13-15
RbI	152	3.9	6-8	7-8	13-16
CsI	44	16.4	7-8	7-8	14-16

the solution, including the solution viscosity and conductivity, as well as the hydrogen bonding network of water molecules, usually exhibit substantial change (Koneshan et al., 1998; Chalikian, 2001; Hancer et al., 2001; Collins, 2004; Nickolov and Miller, 2005; Du and Miller, 2007; Ozdemir et al., 2011). In past decades, significant efforts have been made to understand the relationship between ion hydration states and the flotation behavior of the corresponding salts. And some of the progress will be reviewed briefly in this section.

Structure of hydrated ions. The most striking feature of soluble salts is their high water solubility due to the strong hydration of ions. Table 1 summarizes the solubility of alkali halides in water, as well as the hydration number of corresponding ions as determined from experimental measurements and molecular/quantum simulations (Koneshan et al., 1998b; Varma and Rempe, 2006; Du and Miller, 2007). It is worth noting that due to the strong hydration of alkali halide ions in saturated salt solutions, the number of water molecules are usually deficient to form complete hydration structures around each ion. For example, in the saturated KF solution, the water-to-ion molar ratio is 1.8; however, for all the ions to form independent and complete hydration structures, 12 to 14 water molecules are required. Such a deficiency of water molecules in saturated brine significantly influences the inherent interaction between water molecules and, further, the structure of the hydrogen bonding network.

For aqueous alkali halide solutions, both cations and anions carry a single charge regardless of the ion species and sign of the ion charge. Therefore, the difference in the solution physico-chemical properties is due to the difference in ion size. Figure 1 summarizes the variation of water/water coordination in LiCl, RbCl and CsI solutions from molecular dynamics
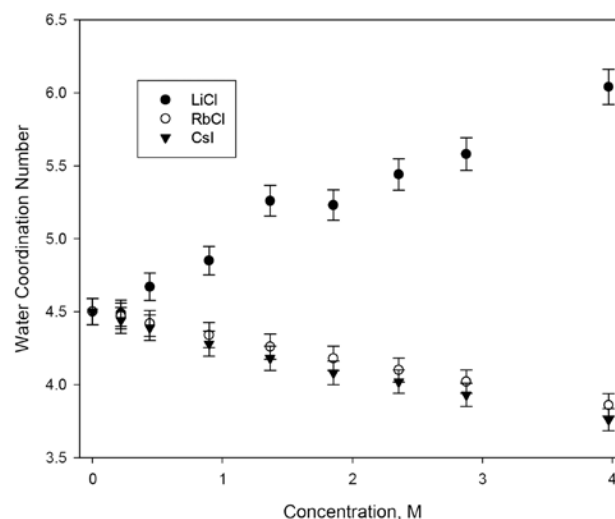

Figure 1 — The first shell water/water coordination numbers in different salt solutions for various solution concentrations (Du et al., 2007).

simulation analysis (Du and Miller, 2007). In pure water, tetrahedral structures of water molecules form dynamic networks, and the average hydration number is 4.5. When Li$^+$ ions are present, the large local electric field binds water molecules in a tetrahedrally coordinated and tightly held hydrophilic hydration shell, in favor of strengthening the water hydrogen bonding network. As more Li$^+$ ions are present, the number of water molecules participating in the hydration of Li$^+$ ions and, in turn, the water/water coordination number, increases with salt concentration.
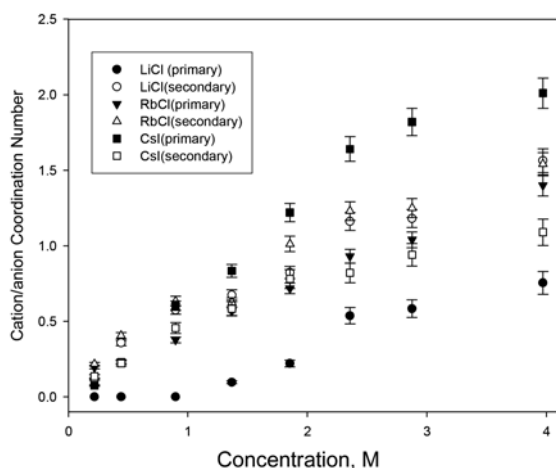
Figure 2 — The coordination number of naked cation/anion pairs (direct cation/anion contact) and hydrated cation/anion pairs (a layer of water between cation/anion pair) in different salt solutions for various solution concentrations (Du et al., 2007).

In contrast, when large Cs^+ ions are in the solution, the local electric fields at the ion surface decrease significantly, and they behave more like uncharged particles (Koneshan et al., 1998b; Du and Miller, 2007). 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, disrupting the integrity of the original water hydrogen bonding network. Thus, the water/water coordination number of these cation-bonded water molecules is less than that of a pure water cluster. As more ions are in the solution, more water molecules will be around ions, and, consequently, as shown in Fig. 1, for large alkali cations the water/water hydration number decreases monotonically with an increase in salt concentration.

The cation/anion coordination number as a function of salt concentration is summarized in Fig. 2, where the primary and secondary coordination numbers are presented. Generally speaking, independent of ion species, the primary and secondary coordination number between cation and anion increases when the salt concentration increases. Specifically, for the Li^+/Cl^- combination, due to the strong local electric fields, water molecules are tightly bonded by Li^+ ions, excluding direct

contact with Cl^- ions and, consequently, 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 number increases much more significantly with concentration, mainly due to loose hydrophobic hydration shells formed around larger Cs^+ ions. Water molecules participating in hydration can be easily be replaced by I^- ions, creating direct cation/anion contact. Consequently, in the CsI solution, the primary coordination number increases faster as a function of salt concentration.

Dynamic properties of hydrated ions. The influence of ion size on solution properties is further revealed from the solution dynamics, which can be studied by analyzing particle residence time and diffusion coefficients as discussed in the following sections (Du and Miller, 2007). The residence time of water in the primary hydration shells of ions and water clusters in different solutions are summarized in Table 2. First, the residence time for water molecules in the water shell increases inversely with ion size for cations and anions. Small ions such as Li^+ ions 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 times.

For large ions such as Cs^+, Rb^+ and I^- ions, the local electric fields are weak, as discussed earlier, and water molecules in the hydration shell are more loosely bonded to them. Thus, they are more mobile, and the residence time of water is shorter. A similar observation has also been documented in the literature (Koneshan et al., 1998b; Chowdhuri and Chandra, 2001). Second, the residence times for the water molecules around Li^+ ions increase significantly with solution concentration, while only a moderate increase was observed for Rb^+ ions, and almost no noticeable change for Cs^+ ions, mainly due to the difference in hydration shell stability of these ions as discussed previously.

The tracer diffusion coefficients for cations, anions and water are shown as a function of salt concentration in Table 3. As seen from Table 3, the diffusion coefficients for the ions and water molecules decrease with increasing salt concentration, and a close examination of the data in Table 3 indicates that, for the CsI solution, the decrease in diffusion coefficients with concentration is the smallest with CsI solution and largest for the LiCl solution. In both cases, as the concentration increases, the diffusion coefficients of the cation and anion become more

Table 2 — Residence times of water molecules around various particles as a function of solution concentration (Du et al., 2007).

	Residence time of water molecule, ps								
Concentration, M	LiCl solutions			RbCl solutions			CsI solutions		
	Li^+	Cl^-	H_2O	Rb^+	Cl^-	H_2O	Cs^+	I^-	H_2O
0.22	50.4	11	5.7	7.7	10.4	5.6	6.8	7.2	5.6
0.44	54.1	11.3	5.7	7.4	9.9	5.6	7.4	7.3	5.5
0.9	64.1	11.5	6.3	8.2	10.3	5.5	7.1	7.3	5.5
1.37	68.5	12.1	6.4	8.1	9.8	5.4	6.9	7.4	5.6
1.85	90.1	13.6	6.6	7.9	10.2	5.5	7	7.1	5.4
2.36	101	14.3	6.9	8.7	10.6	5.8	7.5	7.4	5.8
2.88	108.7	15.8	7.9	8.3	10.2	5.6	7.1	7.5	5.4
3.97	109.9	16.4	7.9	9.1	10.6	5.6	7.5	7.5	5.8

Table 3 — Diffusion coefficients for cations, anions and water shown as a function of salt concentration (Dang, 1995; Koneshan et al., 1998b; Du et al., 2007).

| Concentration, M	Diffusion coefficient, 10^{-9} m²/sec								
	LiCl solutions			RbCl solutions			CsI solutions		
	Li⁺	Cl⁻	H₂O	Rb⁺	Cl⁻	H₂O	Cs⁺	I⁻	H₂O
Dilute solution	1.22	1.77	2.5	1.98	1.77	2.5	1.88	1.6	2.5
0.22	1.06	1.61	2.49	1.86	1.52	2.54	1.77	1.59	2.48
0.44	0.99	1.47	2.49	1.74	1.5	2.52	1.76	1.56	2.49
0.9	0.91	1.28	2.27	1.62	1.46	2.42	1.64	1.48	2.57
1.37	0.8	1.08	2.2	1.52	1.39	2.35	1.62	1.41	2.53
1.85	0.75	0.97	2.07	1.44	1.32	2.31	1.52	1.37	2.51
2.36	0.64	0.87	1.8	1.35	1.21	2.18	1.42	1.28	2.5
2.88	0.58	0.8	1.65	1.25	1.1	2.12	1.27	1.18	2.43
3.97	0.43	0.62	1.44	1.05	1.02	1.97	1.23	1.12	2.35
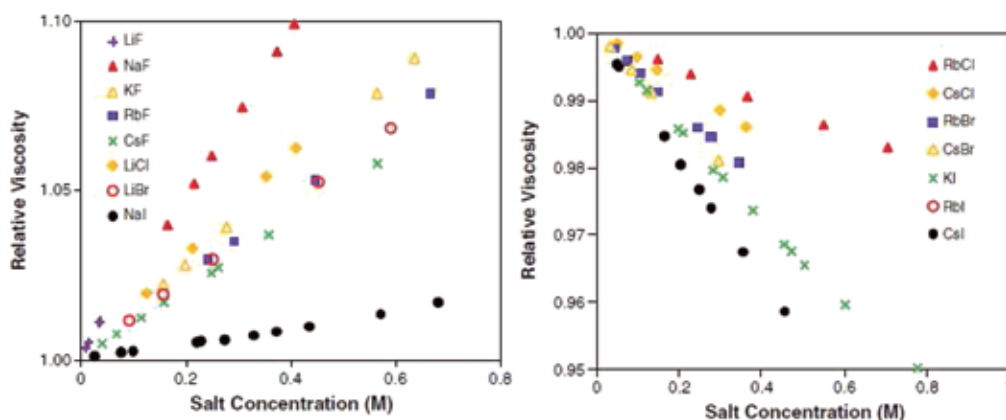
Figure 3 — Measured viscosity (relative to water) of aqueous solutions of kosmotropic (left) and chaotropic (right) salts at 25° C (Ozdemir et al., 2011).

nearly alike. A similar observation has been made in previous studies of aqueous solutions of NaCl and KCl at high concentrations (Allen and Tildesley, 1987; Koneshan and Rasaiah, 2000; Chowdhuri and Chandra, 2001). As for the systems containing large ions (Cs⁺, Rb⁺ and I⁻ ions) with weaker electric fields, the observed decrease of ion diffusivity can also be explained in terms of increased ion pairing, which slows down the movement of ions and water molecules bound to them.

The self-diffusion of water molecules in the LiCl solution changes dramatically in magnitude as the solution becomes denser. The self-diffusion coefficient of extended simple point charge (SPC/E) water at 25° C is 2.5×10^{-9} m²s⁻¹ and decreases by 40% as the concentration of the LiCl solution increases from 0.22 M to 3.97 M (Table 3). Over the same concentration range, the diffusion coefficient of water in CsI solution drops by a factor of only 6%. The decrease in the diffusion coefficient of water with concentration of LiCl again can be attributed to the strong interaction between the Li⁺ ion with water molecules in its hydration shell.

Solution viscosity. The influence of alkali halide ions on solution properties has drawn much research attention, and extensive studies have suggested that, based on alteration of the water hydrogen bonding network, alkali halide ions can be conveniently categorized as either kosmotropes (strongly hydrated) or chaotropes (weakly hydrated) (Collins, 2004).

Further, the ion hydration characteristics can be evaluated by considering the change of solution viscosity with salt concentration.

The influence of ions on the solution viscosity has recently been carefully examined by Ozdemir et al. (2011), and Fig. 3 summarizes viscosities of the selected alkali halide solutions. It is well recognized that the solution viscosity is directly related to the molecular interaction in the fluid and water and the extent of the hydrogen bonding network. When small ions such as Li⁺, Na⁺ and F⁻ are present, water molecules form a stable hydration shell around these ions due to the large charge density, holding the water molecules strongly and, consequently, immobilize the water molecules, creating a "thicker" solution. In contrast, water molecules tend to form a loose hydration shell around large ions such as Rb⁺, Cs⁺, Br⁻ and I⁻ and, instead of being inhibited, the surrounding water molecules are actually being disturbed to a much higher vibrational level, creating a much more "dilute" solution.

The relative viscosity versus concentration is shown in Fig. 4 for solutions of 20 alkali halide salts, determined using the Jones and Dole equation (Jones and Dole, 1929). It is clear from Fig. 4 that 11 of the alkali halides (LiF, NaF, KF, RbF, CsF, LiCl, NaCl, LiBr, NaBr, LiI and NaI) generally result in relative viscosities greater than 1; in other words, they tend to increase the solution viscosity, characteristic of structure-making (kosmotrope) salts. The remaining nine alkali halides
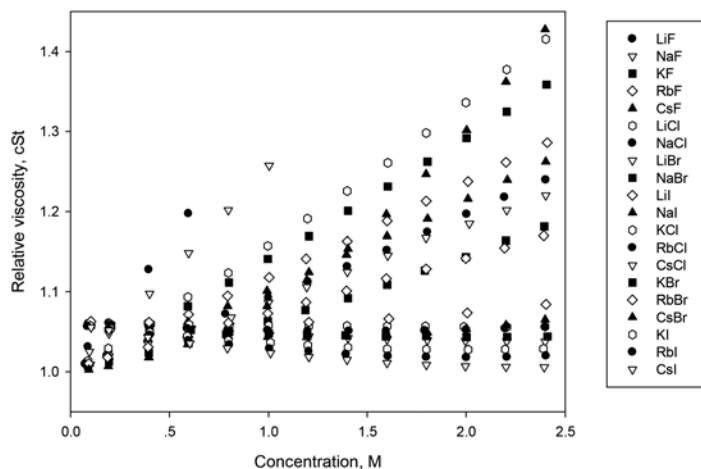
Figure 4 — Viscosity of solutions of the alkali halide salts as a function of concentration (Hancer et al., 2001).

given in Fig. 4 (KCl, RbCl, CsCl, KBr, RbBr, CsBr, KI, RbI and CsI) result in relative viscosities equal to or less than 1, characteristic of structure-breaking (chaotrope) salts. The variation of solution viscosity is in good agreement with experimental measurements, substantiating the influence of ions on solution fluidity (Hancer et al., 2001).

Based on the solution viscosity, alkali halide salts can be conveniently classified as structure-making salts such as NaCl and structure-breaking salts such as CsI (Hancer et al., 2001). Importantly, as will be discussed later, the affinity of ions to surrounding water molecules is directly related to the flotation behavior of the corresponding salts. The viscosity measurements have been further extended to include some other industrially important soluble salts, and the results are summarized in Table 4 (Hancer and Miller, 2000; Cao et al., 2011; Ozdemir et al., 2011). Using solution viscosity as an evaluation criterion, $NaHCO_3$, NH_4HCO_3, and shoenite ($K_2SO_4MgSO_46H_2O$) can, therefore, be regarded as structure breaking salts, whereas $MgCl_2$, Na_2CO_3, K_2CO_3, kainite ($KClMgSO_43H_2O$) and carnallite ($KClMgCl_26H_2O$) are structure-making salts.

Spectroscopic analysis. The effect of ions on water dynamics has been further examined by comparing the hydrogen bonding of water structure using FT-IR vibrational spectroscopy (Nickolov et al., 2003; Nickolov and Miller, 2005; Cao et al., 2011; Ozdemir et al., 2011). Typically, in order to avoid the interference of intermolecular OH interaction, partially deuterated water (5%wt D_2O) was used to study the intermolecular water interaction (Nickolov et al., 2003; Nickolov and Miller, 2005). Figure 5 shows the change of OD vibrational peaks with KF and KI solution concentrations (Nickolov and Miller, 2005). It is clear that the width of the OD band for KF solutions increases significantly, and its peak shifts to lower wavenumbers (blueshift), compared to the OD band in the pure D_2O/H_2O mixture, due to the strong affinity of water molecules for the F^- in the solution (kosmotropic effect), thus enhancing the ice-like structure of water. The opposite tendency is observed in solutions of KI, and the width of the OD band decreases with concentration and its peak shifts to higher wavenumbers (redshift), suggesting that the integrity of the water molecule hydrogen bonding network around large I^- ions has been disturbed

Table 4 — Solubility and relative viscosity of selected soluble salts (Hancer and Miller, 2000; Cao et al., 2011; Ozdemir et al., 2011) .

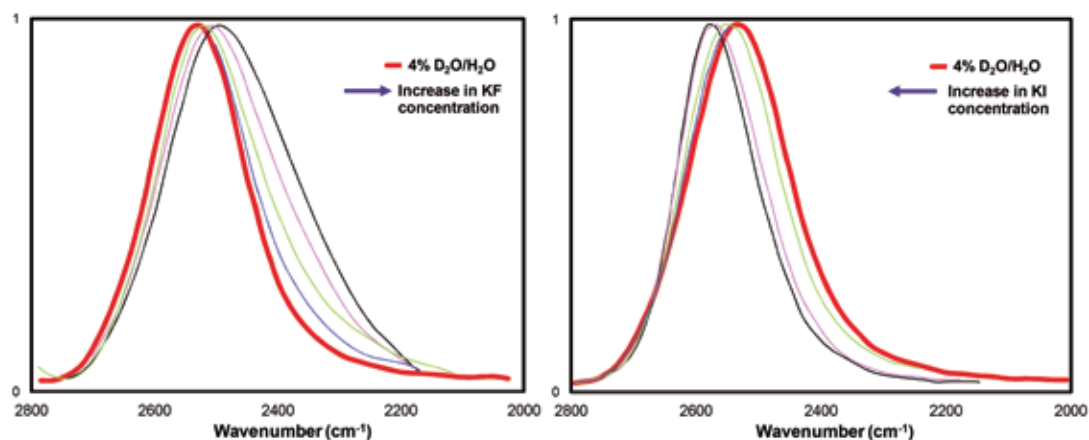| Salt	Solubility, M	Relative viscosity, cSt	Reference
$MgCl_2$	2.5	2.75	(Cao et al., 2011)
Na_2CO_3	2.1	3.8	(Ozdemir et al., 2011)
K_2CO_3	5.0	4.5	(Ozdemir et al., 2011)
$NaHCO_3$	1.2	1.2	(Ozdemir et al., 2011)
NH_4HCO_3	2.2	1.3	(Ozdemir et al., 2011)
Shoenite $K_2SO_4MgSO_46H_2O$	0.8	1.35	(Hancer and Miller, 2000)
Kainite $KClMgSO_43H_2O$	1.5	1.64	(Hancer and Miller, 2000)
Carnallite $KClMgCl_26H_2O$	2.4	1.45	(Hancer and Miller, 2000)

Figure 5 — O-D stretching band spectra of solutions of KF (left) and KI (right) in 4 wt% D_2O in H_2O mixtures depending on concentration. The spectrum of the pure 4 wt% D_2O in H_2O mixture is shown with a thicker line (Nickolov and Miller, 2005).
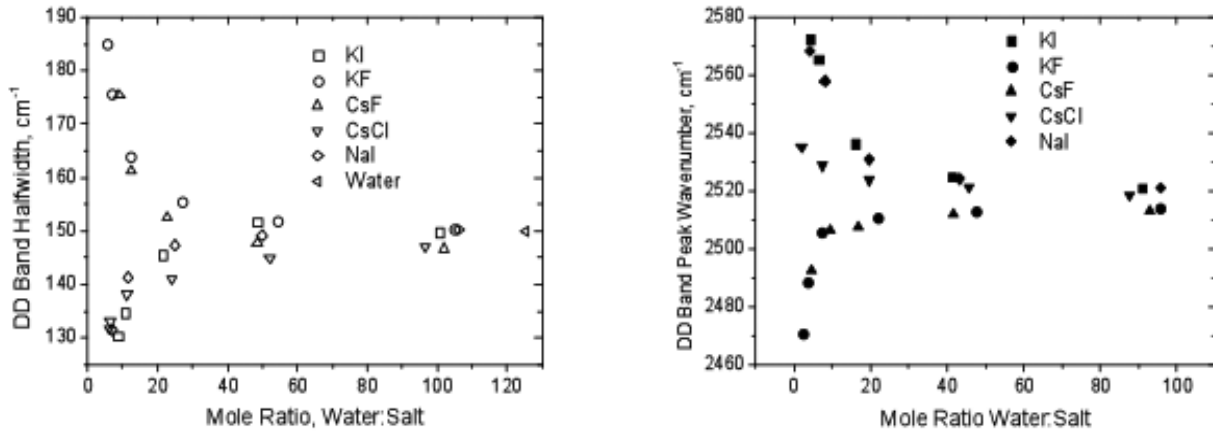
Figure 6 — Dependencies of the OD band full widths at half maximum (left) and peak wavenumber (right) in solutions of alkali halide salts in 4 wt% D_2O in H_2O mixtures depending on mole ratio of water:salt (Nickolov and Miller, 2005).

Table 5 — OD band full widths at half maximum (left) and peak wavenumber (right) in solutions of selected soluble salts (Nickolov et al., 2003; Nickolov and Miller, 2005; Cao et al., 2011; Ozdemir et al., 2011).

Salt	Wavenumber shift direction	Influence on solution viscosity	Water structure maker or breaker	Reference
KF	Low	Increase	Maker	(Nickolov and Miller, 2005)
KI	High	Decrease	Breaker	(Nickolov and Miller, 2005)
CsF	Low	Increase	Maker	(Nickolov and Miller, 2005)
CsCl	High	Decrease	Breaker	(Nickolov and Miller, 2005)
NaI	High	Decrease	Breaker	(Nickolov and Miller, 2005)
Na_2CO_3	Low	Increase	Breaker	(Nickolov et al., 2003; Ozdemir et al., 2011)
$NaHCO_3$	Negligible	Increase	Breaker	(Nickolov et al., 2003; Ozdemir et al., 2011)
Bischofite $MgCl_2 6H_2O$	Low	Increase	Maker	(Cao et al., 2011)
Carnallite $KClMgCl_2 6H_2O$	Low	Increase	Maker	(Cao et al., 2011)

(chaotropic effect) (Nickolov and Miller, 2005).

Figure 6 summarizes the values of the full widths at half maximum and the peak wavenumbers of the OD band for selected salt solutions, and the influence of different salts on the variation of the OD band is obvious (Nickolov and Miller, 2005). In KF and CsF solutions, when the solution concentration is high (small water to salt mole ratio), band width increase and band peak wavenumber blueshift occur, suggesting that the water hydrogen bonding network has been strengthened due to the kosmotropic effect of the F⁻ ion. On the other hand, when large Cl⁻ and I⁻ ions are present in solution, the integrity of the water hydrogen bonding network will be disturbed, creating chaotropic states, as evidenced by the decrease of the OD band width and redshift of the band peak wavenumber.

Table 5 includes some of the literature results with respect to the influence of soluble salts on the molecular vibration of water molecules (Nickolov et al., 2003; Nickolov and Miller, 2005; Cao et al., 2011; Ozdemir et al., 2011). It is evident that the influence of salts on the OH vibrational level can be correlated with their influence on the solution viscosity, an increased solution viscosity is always associated with an inhibition of OH vibration, as suggested by the shift of OD stretching vibration bands to low wavenumbers (blue shift).

Table 6 — Correlation of the flotation response of alkali halide salts using either DAH or SDS with water structure (Hancer et al., 2001).

Ion	F⁻	Cl⁻	Br⁻	I⁻
Li⁺	F	NF	NF	NF
	STRUCTURE MAKERS			
Na⁺	NF	NF	NF	NF
	STRUCTURE BREAKERS			
K⁺	NF	F	F	F
Rb⁺	NF	F	F	F
Cs⁺	NF	F	F	F

Correlation of water structure with salt flotation. Hancer et al. (2001) studied the flotation behavior of selected alkali halide salts using dodecylamine hydrochloride (DAH) and sodium dodecylsulfate (SDS) as collectors, and found that the structure-breaking salts can be very well floated regardless of the salt particle surface charge, and structure-making salts showed no evidence of flotation at all. Consequently, a theory based

Table 7 — Steric and hydration effect for alkali and halide ions (Veeramasuneni et al., 1997).			
Group	Steric effect	Hydration effect	Alkali halide
A	Small $r^+ \sim r_w$ $r^- / r^+ < 1.4$	Small $n_h{}^+ / n_h \leq 2$	KF, RbF, CsF, CsCl, CsBr, CsI
B	Significant $r^+ < r_w$ $r^- / r^+ > 1.4$	No; behavior limited by steric effect	LiF, NaF, LiCl, NaCl, LiBr, NaBr, LiI, NaI, KI
C	Small $r^+ \approx r_w$ $r^- / r^+ > 1.4$	Significant $n_h{}^+ / n_h \geq 2$	KCl, RbCl, KBr, RbBr, RbI

on the affinity of salt to water molecules has been proposed as illustrated in Table 6 (Hancer et al., 2001). The essence of this theory is that structure-making salts contain ions that can interact strongly with surrounding water molecules, consequently forming stable hydration shells, and such phenomena occurs in the bulk solution and the salt mineral surface as well, which will be discussed in section 4, "Wetting characteristics of soluble salts." Under such circumstances, a very stable hydration layer will be established at the salt particle surface even in saturated brine, inhibiting the adsorption of collector molecules/colloids at the salt surface. Hence, no hydrophobic state will be created and, consequently bubble attachment and flotation will not occur. In contrast, structure-breaking salts are composed of ions that exhibit a chaotropic effect on surrounding water molecules, disturbing the water hydrogen bonding network. The water molecules at the salt surface are neither strongly bonded with the ions due to the lack of enough electrostatic attraction, nor strongly bonded with surrounding water molecules due to the partial disruption of the water hydrogen bonding network. In this regard, the replacement of interfacial water molecules by collector molecules/colloids can be realized, facilitating the bubble particle attachment and the flotation of salt minerals.

Surface charge of soluble salts

The surface charge of mineral particles in suspension is of significant interest in many flotation systems, influencing collector adsorption and particle interactions. In this regard, examination of the surface charge of soluble salts in their saturated brine should be considered in the analysis of their flotation behavior. Some of the progress that has been achieved in the past two decades is discussed in the following section.

Theory. As previously discussed, one of the distinct features of the soluble salt flotation system is the solubility of the salt minerals, and the dissolution/crystallization of ions at the salt surface. However, due to the difference in the hydration energy of ions, the salt mineral surfaces are expected to be partially charged, even in their saturated brines. The surface charge of soluble salts can be predicted by the lattice ion hydration theory, and for nonreactive ionic uni-univalent salts such as alkali halides, the surface charge can be estimated simply from a comparison of the hydration free energies of the corresponding gaseous ions (Miller et al., 1992; Miller and Yalamanchili, 1994). For example, if the hydration free energy of the surface lattice cation is more negative than that of the surface lattice anion, then the surface will carry a negative charge. The converse is also true. The simplified lattice ion hydration (SLIH) theory can be represented for the cation by summing Eqs. (1) and (2):

$$M_s{}^+ \rightarrow M_g{}^+, \text{ surface binding energy} \quad (1)$$

$$M_g{}^+ \rightarrow M_{aq}{}^+, \text{ gaseous ion hydration free energy} \quad (2)$$

$$M_s{}^+ \rightarrow M_{aq}{}^+, \text{ energy for hydration of surface ion} \quad (3)$$

The same reactions can be written for the anion. Based on this theory, Miller et al. (Miller et al., 1992; Yalamanchili and Miller, 1994) have systematically analyzed the surface charges of the complete alkali halide salt series and found seven exceptions (LiF, NaCl, KCl, KBr, RbBr, KI and RbI) that showed deviation from the nonequilibrim electrophoretic laser-Doppler electrophoresis measurements, to be discussed in the following section. Further investigation of the salt surface characteristics reveals that ions at the salt surface are partially hydrated and, due to the difference in ion radius (steric effect) and ion hydration number (hydration effect), improvement of the simplified lattice ion hydration theory has to be made to predict the surface charge more accurately. Consequently, Veeramasuneni et al. (1997) developed the extended lattice ion hydration (ELIH) theory by taking into consideration the partial hydration of surface ions. For a uni-univalent ionic solid, MX:

$$M_{s(ph)}{}^+ \rightarrow M_{s(f)}{}^+, w_{i-d}(M^+) \quad (4)$$

$$M_{s(f)}{}^+ \rightarrow M_g{}^+, \Delta U_s(M^+) \quad (5)$$

$$M_g{}^+ \rightarrow, M_{aq}{}^+, \Delta F_h(M^+) \quad (6)$$

$$M_{s(ph)}{}^+ \rightarrow M_{aq}{}^+, \Delta G_h(M^+) \quad (7)$$

where subscripts *s(ph)*, *s(f)*, *g* and *aq* represent the partially hydrated surface state, free (vacuum) surface state, gaseous state and aqueous state, respectively. $w_{i-d}(M^+)$, $\Delta U_s(M^+)$ and $\Delta F_h(M^+)$ are the ion-dipole interaction energy, surface binding energy and the gaseous hydration energy, respectively. Therefore, the hydration free energy of the surface cation M^+ can be calculated as:

$$\Delta G_h(M^+) = \Delta U_h(M^+) + \Delta H_h(M^+) + \Delta w_{i-d}(M^+) \quad (8)$$

A similar approach can also be applied to calculate the surface anion hydration free energy. The ion-dipole interaction energy, $w_{i-d}(M^+)$, can be calculated using the following equation:

$$w_{i-d} = \frac{zeu\cos\theta}{4\pi\varepsilon_0\varepsilon r^2} \quad (9)$$

where *z* is valency, *e* is electronic charge, *u* is water dipole moment, ε_0 is permittivity of free space and ε is the dielectric constant of the media. The angle θ as well as the distance *r* are dependent on the size and the hydration number of ions. Alkali halide salts can, therefore, be categorized into three

Alkali	$\Delta G_h{}^g$(KJ·mol^{-1})	$\Delta w_{i\text{-}d}$ (KJ·mol^{-1})	$\Delta G_h = \Delta G_h{}^g + \Delta w_{i\text{-}d}$	Sign of surface charge		
				Prediction[a]	Prediction[b]	Experiment[c]
LiF	-9.62	60.7	51.08	-	+	+
NaF	89.54	58.74	148.28	+	+	+
KF	162.76	9.28	172.04	+	+	+
RbF	184.52	13.64	198.16	+	+	+
CsF	216.73	18.58	235.31	+	+	+
LiCl	-121.34	39.67	-81.67	-	-	-
NaCl	-22.6	39.29	16.69	-	+	+
KCl	48.95	-45.49	3.46	+	+	-
RbCl	70.71	-46.43	24.28	+	+	+
CsCl	102.92	-2.42	100.5	+	+	+
LiBr	-152.3	35.27	-117.03	-	-	-
NaBr	-53.14	35.14	-18	-	-	-
KBr	20.08	-58.36	-38.28	+	-	-
RbBr	41.89	-52.48	-10.91	+	-	-
CsBr	74.05	-7.13	66.92	+	+	+
Lil	-191.63	29.61	-162.02	-	-	-
Nal	-92.47	29.78	-62.69	-	-	-
KI	-19.25	30.11	10.86	-	+	+
Rbl	2.51	-44.3	-41.79	+	-	-
Csl	34.72	-13.32	21.4	+	+	+

Table 8 — The sign of the surface charge for alkali halide salts (Miller et al., 1992; Veeramasuneni et al., 1997).

[a] Simplified lattice ion hydration theory.

[b] Extended lattice ion hydration theory.

[c] Electrophoretic-mobility measurements by laser-Doppler electrophoresis.

groups, as shown in Table 7.

Using the extended lattice ion hydration theory, the surface charge of alkali halide salts has been predicted, and the results are summarized in Table 8. It is evident that the predicted sign of the surface charge is in good agreement with values obtained from nonequilibrium electrophoretic measurements by laser-Doppler electrophoresis. The one exception is KCl, whose anomalous behavior is due to oxygen defects (Veeramasuneni et al., 1996). If oxygen defects are removed from KCl, the sign of the surface charge is reversed from negative to positive and the experimental results agree with the theoretical prediction.

Experiment. Mineral particle surface charge measurements are typically realized from electrophoretic-mobility measurements. However, this technique is limited to relatively low ionic strength ($I < 10^{-2}$M) due to electrode polarization, conductivity limitation and the generation of thermal induced convective flow in the sample capillary. In this regard, traditional electrophoresis measurements are unable to provide satisfactory results for soluble salt particles that are only stable in saturated brine with extremely high ionic strength (Miller et al., 1992). In addition, the electrical double layer at salt surfaces will be completely compressed in saturated brine, creating an extra challenge for accurate surface charge measurement for salt particles under equilibrium conditions. To overcome such problems, Miller et al. (1992) have used the laser-Doppler technique to determine the electrophoretic mobility of soluble salt crystals under nonequilibrium conditions, and obtained valuable information regarding the surface charge of alkali halides and other soluble salts. Table 9 summarizes the nonequilibrium electrophoretic mobilities for the alkali halides. As discussed in the previous section, the sign of the surface charge of alkali halide particles is well predicted using the extended lattice ion hydration theory, complementing the experimental results reported in Table 9.

In addition to theoretical prediction and experimental measurements, further efforts have been made by Du et al. (Du and Miller, 2007) using molecular dynamics simulation (MDS) analysis. Table 10 summarizes the results from MDS analysis, and excellent agreement has been achieved, suggesting MDS as a valid method for the examination of soluble salt surface charges. The difference in the sign of the surface charge regarding KCl has been carefully examined by Veeramasuneni et al. (1996) and found to be due to the bulk oxygen defects associated with such salts.

Correlation of surface charge with flotation. As mentioned previously, adsorption of collector molecules due to the attraction of charged mineral surfaces to the collector polar groups is always an attractive and convenient approach in explaining the collector adsorption mechanism; therefore, it is not surprising to notice such efforts have been made to explain soluble salt flotation systems. Miller et al. (1992) in their early study of the flotation behavior of KCl and NaCl using DDA and sodium laurate have noticed that the cationic collector, DDA, can selectively float negatively charged KCl, and the anionic collector, sodium laurate, exhibits strong selectivity in floating positively charged NaCl. Such observation appears to support the adsorption theory based on the salt surface charge very well. However, further study using the anionic collector, SDS, has shown that, KCl can be effectively floated, and no flotation of NaCl has been realized, in contradiction to the surface charge theory (Hancer et al., 2001). Later research further proved

Table 9 — Surface charge results of alkali halide salts from nonequilibrium laser-Doppler electrophoresis experiments (Miller et al., 1992).

Alkali halide	Electrophoretic mobility, µm/(sV·cm)	
	Range	Mean
Fluorides		
LiF	+0.175 to +0.271	+0.221
NaF	+0.112 to +0.171	+0.162
KF	+0.061 to +0.083	+0.084
RbF	+0.04 to +0.135	+0.065
CsF	+0.486 to +0.813	+0.582
Chlorides		
LiCl	-0.497 to -0.733	-0.641
NaCl	+0.124 to +0.216	+0.163
KCl	-0.33 to -0.467	-0.421
RbCl	+0.164 to +0.27	+0.213
CsCl	+0.325 to +0.495	+0.397
Bromides		
LiBr	-0.224 to -0.375	-0.32
NaBr	-0.252 to -0.342	-0.311
RbBr	-0.388 to -0.496	-0.459
KBr	-0.078 to -0.106	-0.086
CsBr	+0.064 to +0.081	+0.072
Iodides		
LiI	-0.741 to -0.803	-0.761
NaI	-0.662 to -0.791	-0.741
KI	+0.057 to +0.109	+0.079
RbI	-0.098 to -0.348	-0.253
CsI	+0.025 to +0.061	+0.041
NaI·2H$_2$O	+0.026 to +0.05	+0.039

addition, the collector is surrounded by counter ions, neutralizing the polarity. Therefore, adsorption due to electrostatic attraction cannot be such an important issue.

Wetting characteristics of soluble salts

Mineral surface wetting characteristics is another important issue in discussing flotation chemistry, and information with respect to surface hydration is often directly associated with collector adsorption states, especially if the adsorption involves hydrophobic interactions and hydration phenomena. From the previous discussions, it is recognized that ions in solution exhibit quite different hydration behavior, and such behavior has been related to the flotation responses of corresponding salts, considering that the ions at the surface hold hydration states similar to that in bulk solution. In this section, some of the findings regarding the hydration states of soluble salts will be discussed.

Contact angle. Soluble salts are composed of ions that can be easily hydrated, and wetting of the salt surfaces usually occurs instantaneously when the salt is in contact with water. However, depending on the size and charge, different ions exhibit a substantial difference in hydration state. For example, the Li$^+$ ion can form a very stable tetrahedral hydration structure with four water molecules, and the stability of such a structure is significantly greater than that of the hydration structure for a water molecule. Even though carrying the same charge as Li$^+$, Cs$^+$ behaves in a manner similar to an uncharged particle due to its low charge density, and can only create a very loose hydration shell (Koneshan et al., 1998b; Du and Miller, 2007). Therefore, understanding the hydration characteristics of constituent ions is of particular importance in describing the wetting characteristics of soluble salts.

Contact angle measurements using sessile drop and captive bubble techniques are most widely applied to study solid surface wetting characteristics, and significant efforts have been made in the past two decades to examine different soluble salt minerals. Table 12 summarizes the advancing contact angle for selected soluble salt crystals in their saturated solutions in the absence of collectors (Hancer and Miller, 2000; Hancer et al., 2001; Ozdemir et al., 2009; Ozdemir et al., 2011). It is important to note that there is a general agreement with respect to the ion hydration states in the bulk solution and for the corresponding salt mineral surfaces. Even more significant is that these structural characteristics of interfacial water are revealed from contact angle measurements in the absence of collectors. On the basis of contact angle measurement results, it is observed that the interfacial water at a structure breaker salt surface (e.g., KI) has less stability because the ions at the surface tend to create chaotropic states due to the weak ion/water interactions. In contrast, water molecules will be immobilized by structure-maker salts such as NaCl, which results in complete wetting of the salt surface, as evidenced by the zero contact angle.

that the surface charge theory does not explain the soluble salt flotation behavior, and some results are summarized in Table 11 (Hancer et al., 1997; Ozcan and Miller, 2002; Cao et al., 2010; Ozdemir et al., 2011). It is interesting to note that, regardless of surface charge, the flotation behavior of the selected soluble salts using DAH and SDS follow the same trend; that is, if the salt can be floated using DAH, it can also be floated using SDS. The reverse statement also holds true, substantiating the conclusion that the charge of the salt mineral surface does not have a significant influence on soluble salt flotation.

The failure of the surface charge theory is easily understood by considering the fact that soluble salt flotation usually occurs in saturated brine with extremely high ionic strength, and the electrical double layer will be completely compressed. In

Table 10 — Sign of surface charge of selected alkali halide salts.

Salt	Surface charge		
	MDS (Du and Miller, 2007)	Analytical model (Veeramasuneni et al., 1997)	Experimental results (Miller et al., 1992)
LiCl	-	-	-
NaCl	+	+	+
KCl	+	+	-
RbCl	+	+	+

Table 11 — Surface charge of selected soluble salts and their flotation response.

Salt	Electrophoretic mobility, (μ/s)/(V/cm)	Surface charge	Flotation DAH	Flotation SDS	Reference
LiF	+0.22 ± 0.15	+	Yes	Yes	(Hancer et al., 2001)
NaCl	+0.19 ± 0.10	+	No	No	(Hancer et al., 2001; Cao et al., 2010)
NaF	+0.16 ± 0.12	+	No	No	(Hancer et al., 2001)
CsI	+0.05 ± 0.04	+	Yes	Yes	(Hancer et al., 2001)
KI	+0.08 ± 0.06	+	NA	NA	(Hancer et al., 2001)
KCl	-0.47 ± 0.26	-	Yes	Yes	(Hancer et al., 2001; Cao et al., 2010)
$KClO_4$	-0.88 ± 0.40	-	Yes	Yes	(Hancer et al., 2001)
K_2SO_4	-0.62 ± 0.13	-	Yes	Yes	(Hancer et al., 2001)
KNO_3	-0.52 ± 0.16	-	Yes	Yes	(Hancer et al., 2001)
Na_2CO_3	-0.91 ± 0.23	-	No	No	(Ozcan and Miller, 2002; Ozdemir et al., 2011)
$NaHCO_3$	-1.16 ± 0.31	-	Yes	Yes	(Ozcan and Miller, 2002; Ozdemir et al., 2011)
$NaNO_3$	-0.86 ± 0.56	-	No	No	(Hancer et al., 2001)
$Na_2SO_4 \cdot 10H_2O$	-1.17 ± 0.15	-	Yes	NA	(Hancer et al., 1997)
$Na_2B_4O_7 \cdot 10H_2O$	-1.68 ± 0.1	-	Yes	Yes	(Ozdemir et al., 2011)

Table 12 — Contact angles of brines at selected soluble salt surfaces (Hancer and Miller, 2000; Hancer et al., 2001; Ozdemir et al., 2009; Ozdemir et al., 2011).

Salt	Contact angle, degrees	Water structure maker or breaker	Reference
KI	25 ± 2 (12 ± 1.4)	B	(Hancer et al., 2001)
KCl	7.9 ± 0.5	B	(Hancer et al., 2001)
NaCl	0	M	(Hancer et al., 2001)
NaF	0	M	(Hancer et al., 2001)
$KClO_4$	28.4 ± 2	-	(Hancer et al., 2001)
K_2SO_4	20.1 ± 2	-	(Hancer et al., 2001)
KNO_3	15.0 ± 1	-	(Hancer et al., 2001)
Na_2CO_3	0	M	(Ozdemir et al., 2009; Ozdemir et al., 2011)
$NaHCO_3$	19.8	B	(Ozdemir et al., 2009; Ozdemir et al., 2011)
Trona $Na_2CO_3NaHCO_32H_2O$	0.4	M	(Ozdemir et al., 2009; Ozdemir et al., 2011)
Shoenite $K_2SO_4MgSO_46H_2O$	15 ± 2	B	(Hancer and Miller, 2000)
Kainite $KClMgSO_43H_2O$	0	M	(Hancer and Miller, 2000)
Carnallite $KClMgCl_26H_2O$	0	M	(Hancer and Miller, 2000)

The influence of collector molecules on contact angle has been examined to understand the nature of collector adsorption, and some of the results for KCl and NaCl are illustrated in Fig. 7 (Cao et al., 2010). It is clear that both anionic and cationic collectors absorb at the KCl surface, as evidenced by the increased contact angle with collector concentration. However, no collector adsorption appears to occur at the NaCl surface, as suggested by the zero contact angle. Such observation has been used to explain the selective flotation separation of KCl from NaCl using alkyl amine and alkyl sulfate collectors. The inability of NaCl to adsorb collectors has been attributed to surface hydration and the strong interfacial water structure, inhibiting the adsorption of the collector molecules (Celik et al., 2002; Cao et al., 2010).
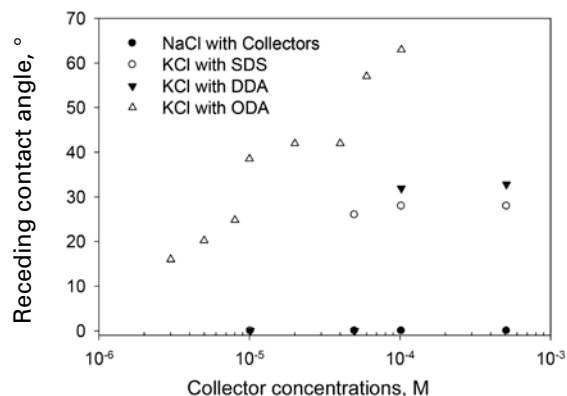
Bubble attachment time. To complement contact angle

Figure 7 — Captive bubble contact angles of saturated brines at KCl and NaCl salt surfaces with the addition of different collectors (Cao et al., 2010).

Legend:
- NaCl with Collectors
- KCl with SDS
- KCl with DDA
- KCl with ODA

Table 13 — Bubble attachment time of selected soluble salts (Cao et al., 2010; Ozdemir et al., 2010).

Collector concentration, M	Attachment time, ms			
	KCl	NaCl	NaHCO$_3$	Na$_2$CO$_3$
DAH				
No collector	2,000	NA	1,800	NA
1×10^{-6}	1,700	NA	1,800	-
5×10^{-6}	600	NA	-	-
8×10^{-6}	60	NA	-	-
1×10^{-5}	50	NA	270	NA
5×10^{-5}	-	-	100	NA
1×10^{-4}	-	-	45	NA
SDS				
No collector	2,000	NA	1,800	NA
1×10^{-6}	1,800	NA	1,800	-
5×10^{-6}	-	-	-	-
8×10^{-6}	190	NA	-	-
1×10^{-5}	100	NA	200	NA
5×10^{-5}	37	NA	60	NA
1×10^{-4}	-	-	40	NA

measurements, bubble attachment time experiments can also be carried out to characterize the hydrophobicity of mineral particles either in their natural state or with collector addition. Cao et al. and Ozdemir et al. studied the bubble attachment time for selected alkali halide salts with DAH, and the results are summarized in Table 13 (Cao et al., 2010; Ozdemir et al., 2010; Ozdemir et al., 2011). The measurements appear to suggest that no collector adsorption occurs at the surface of
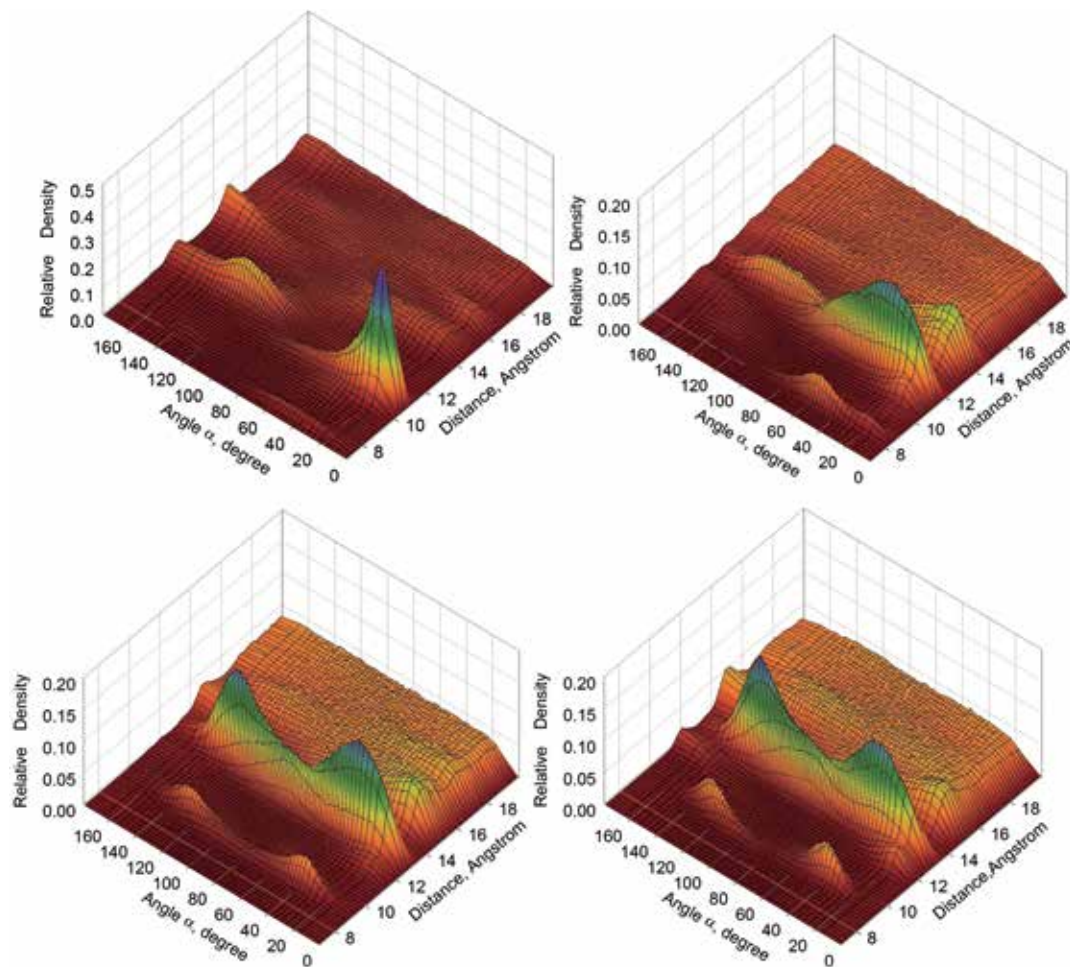

Figure 8 — Angle of water dipole moment with respect to surface normal along LiCl (upper left), NaCl (upper right), KCl (lower left) and RbCl (lower right) salt surface normals (Du and Miller, 2007).
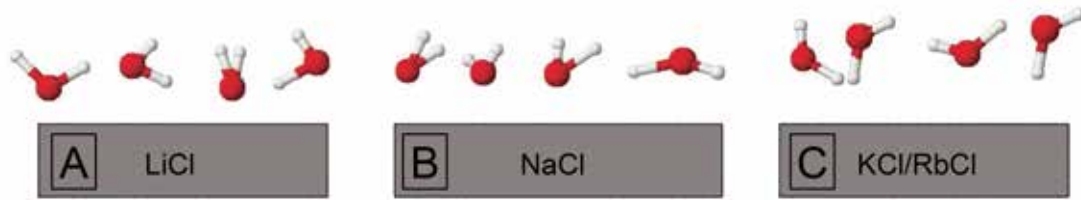
Figure 9 — Schematic drawing of water molecules at LiCl, NaCl, KCl and RbCl crystal surfaces in their saturated brines (Du and Miller, 2007).

structure-making salts (NaCl and Na_2CO_3). On the other hand, anionic and cationic collectors have a tendency to adsorb at the surface of structure breaking salts (KCl and $NaHCO_3$).

Molecular dynamics simulation (MDS) analysis. Du et al. (Du and Miller, 2007) have studied the wetting characteristics of soluble salt mineral surfaces using MDS analysis, which is able to provide additional information to understand the interaction between the surface ions and the water molecules. The interfacial water dipole moment distribution analysis is very helpful in explaining the surface ion hydration states. Figure 8 describes the angle of the water dipole moment with respect to surface normal profiles for LiCl, NaCl, KCl and RbCl, respectively. It is observed that for the LiCl surface, there is a sharp peak, suggesting that the surface water molecules exhibit specific orientation due to the strong interaction with the Li^+ ion. At the NaCl surface, due to decreased Na^+/water interaction, water molecules exhibit more orientation flexibility as suggested by the broad peak. With further increase in the cation size, some dramatic changes are observed, as is the case for the KCl system. The two peaks in the water dipole distribution are mainly due to the balance between the weaker K^+ ion/oxygen and Cl^- ion/hydrogen interactions, suggesting that these two interactions are of comparable magnitude. At the RbCl crystal surface, the results are similar to those observed at a KCl crystal surface.

Figure 9 demonstrates the orientation of water molecules at salt surfaces. As clearly seen for the LiCl and NaCl surfaces, water oxygen is preferentially closer to the surface due to the strong cation/oxygen interaction, whereas at the KCl and RbCl surfaces, water hydrogens are closer to the surface due to the balance of interactions between cation/oxygen and anion/water.

The hydrogen bonding between water molecules is an important issue in the study of surface hydration states. Table 14 summarizes the variation of the water hydrogen bonding number (n_{HB}) in different brine solutions as a function of distance to salt surfaces (Du and Miller, 2007). The variation of n_{HB} in different salt solutions is understood in terms of water/ion interactions. In saturated solutions, due to the presence of a large number of ions (in solution and at the salt surface), almost all water molecules participate in ion hydration, and exhibit different behavior than they do in pure water. Generally speaking, for water molecules in an ion hydration shell, one or more bonding sites have been taken by the corresponding ions, resulting in a decrease of n_{HB} in brine solution when compared to pure water.

Specifically, around small cations such as Li^+ and Na^+, hydrophilic hydration shells are formed (Koneshan et al., 1998a; Du et al., 2007) due to strong cation/water interactions. Under these conditions, neighboring water molecules in a hydration shell are not be able to be aligned to the right angle that satisfies the requirement for hydrogen bond formation due to the strong cation/oxygen attraction and cation/hydrogen repulsion

Table 14 — Summary of water hydrogen bonding number (n_{HB}) at selected alkali chloride salt crystal surfaces in saturated solutions (Du and Miller, 2007).

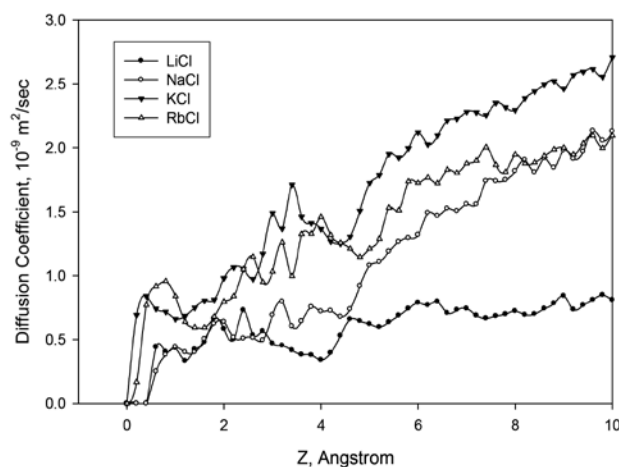| Salt	Water hydrogen bonding number	
	Primary water layer	**Bulk water**
LiCl	0.48	0.65
NaCl	1.06	1.7
KCl	1.34	1.98
RbCl	1.22	1.71

Figure 10 — Comparison of water diffusion coefficients along surface normals for different alkali chlorides (Du and Miller, 2007).

(Du et al., 2007).

In contrast, hydrophobic hydration shells are formed around large cations such as the K^+ and Rb^+ ions (Koneshan et al., 1998b; Du et al., 2007), and water molecules in the hydration shells try to minimize the number of dangling hydrogen bonds by hydrogen bonding with neighboring water molecules, forming cages around these ions (Chalikian, 2001; Chandler, 2005). Consequently, the hydrogen bonding number in KCl and RbCl solutions is higher than that in LiCl and NaCl solutions.

Further, due to the packing of ions more densely at the salt mineral surface than in the bulk solution, the water hydrogen bonding number at the surface is smaller than that in the bulk solution, suggesting that the hydration of ions is more significant at the salt surface. The strong hydration of surface ions will inevitably influence the collector adsorption at the salt surface, and the stronger the hydration, the greater the energy needed to replace the interfacial water molecule and stabilize adsorption. This theory has been used to explain the selective flotation of KCl from NaCl using DAH or SDS with

Table 15 — Comparison of water surface residence time and self-diffusion coefficients in saturated solution at different distances from the surface for selected alkali chloride crystals (Du and Miller, 2007).

Salt	Residence time, ps		Diffusion coefficient, 10^{-9} m²/sec	
	Primary water layer	Bulk water	Primary water layer	Bulk water
LiCl	102	44	0.61	0.78
NaCl	32.5	7.7	1.08	1.9
KCl	14.8	5.9	1.65	2.42
RbCl	16.5	6.8	1.39	1.93

great success, which will be further discussed later. On the other hand, there exists another possibility that if interfacial water is stabilized by bonding with surface ions, then, instead of replacing the surface water molecules, certain collector molecules could be adsorbed at the salt surface via hydrogen bonding with interfacial water molecules, which could explain the flotation of NaCl using dodecylmorpholine and sodium laurate as collectors (Miller et al., 1992; Titkov, 2004).

The self-diffusion coefficients for water molecules at LiCl, NaCl, KCl and RbCl salts are shown as a function of distance from the surface in Fig. 10. First of all, in general, water molecules in KCl and RbCl saturated solutions diffuse significantly faster than they do in NaCl and LiCl saturated solutions. 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; Koneshan et al., 1998a; Koneshan and Rasaiah, 2000; Chowdhuri and Chandra, 2001; Du et al., 2007). Secondly, the self-diffusion coefficient for water molecules in the salt/water interfacial region is significantly lower than that in bulk water. For 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. Third, the diffusion of water molecules in bulk shows a strong concentration dependence. In saturated LiCl solutions ($\sim$14 M), the self-diffusion coefficient of water molecules in the bulk solution ($\sim$0.8 x 10^{-9} m²/sec) is significantly lower than the self-diffusion coefficient in pure water ($\sim$2.5 x 10^{-9} m²/sec) (Berendsen et al., 1987; Du et al., 2007) due to the large concentration of ions (especially Li$^+$ ions) which interact strongly with water molecules and immobilize them. In contrast, in KCl saturated solutions ($\sim$4.8 M), the water self-diffusion coefficient in bulk solution ($\sim$2.5 x 10^{-9} m²/sec) is similar to the value for pure water.

To understand how tightly water molecules are bonded to the salt surface, and how long a water molecule will stay in each water layer, the residence time of water molecules along the salt surface normal has been calculated, and the results are summarized in Table 15. For comparison, the corresponding self-diffusion coefficients of water molecules are present in Table 15.

For water molecules in the interfacial region, their residence time shows a clear cation dependence as $\tau_{LiCl} > \tau_{NaCl} > \tau_{KCl} \approx \tau_{RbCl}$, due to the fact that small cations such as Li$^+$ and Na$^+$ interact more strongly with water molecules 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 compared to water molecules at crystal lattice positions and interfacial water molecules as indicated by the short residence times and large diffusion coefficients. For water molecules in bulk KCl solution, the residence time (5.9 ps) and self-diffusion coefficient ($\sim$2.5 x 10^{-9} m²/sec) are very close to the value for pure water ($\sim$5 ps and $\sim$2.5 x 10^{-9} m²/sec, respectively) (Berendsen et al., 1987; Koneshan et al., 1998b; Du et al., 2007).

Correlation of salt surface hydration states with flotation. Previous research regarding soluble salt flotation has suggested that interfacial water structure plays a significant role in surfactant adsorption (Hancer et al., 2001). For example, even in the absence of a collector, "structure breaking" salts such as KCl and KI have been shown to have some hydrophobic character, whereas "structure making" salts are completely wetted by their saturated brine, as suggested from both contact angle measurements, bubble attachment time measurements and MDS analysis.

It can be noticed that there is a systematic decrease in contact angle as the ion size in the solution increases. The NaCl and NaF salt surfaces are totally hydrated, as suggested by the zero contact angles. In contrast, KI and KCl appear to be less hydrated, as indicated by the finite contact angles (Hancer et al., 2001; Cao et al., 2010; Ozdemir et al., 2011). The MDS results complement the contact angle measurement results well. According to our MDS study, due to different cation sizes and, consequently, different magnitudes of the local electric field, water structures at different alkali chloride crystal surfaces are different. At the LiCl and NaCl surfaces, water molecules are highly ordered, as suggested by the particular orientations of interfacial water as discussed previously. The structure of water molecules at "structure making" salt surfaces, due to the strong interaction between the water molecules and surface lattice ions (especially cations), suggests a very stable thermodynamic state, which is confirmed by the small self-diffusion coefficients and long residence times of interfacial water molecules. When surfactant molecules are present, replacement of surface water should be energetically unfavorable. Therefore, adsorption is not expected, despite the sign of the salt crystal surface charge.

On the other hand, the organization of water molecules at the KCl and RbCl crystal surfaces shows obvious randomness because of the relatively weak water/surface ion interactions. This is confirmed by the finite contact angles (Hancer et al., 2001), as well as large interfacial water diffusion coefficient and short residence times from MDS analysis. The less ordered interfacial water structure being an energetically less stable state, suggests that surfactant adsorption would be possible with sufficient hydrophobicity created for bubble attachment and subsequent flotation.

Flotation chemistry of soluble salts

As discussed in the introduction section, significant efforts have been made to understand the flotation chemistry of soluble salts in their saturated brines, and respective theories from different perspectives have been developed. However, due to the complexity of this system, a theory that can provide the perfect answer for all the soluble salt flotation systems has yet to be established. In this section, some of the more successful theories in explaining collector adsorption and flotation behavior of industrially important soluble salt minerals are
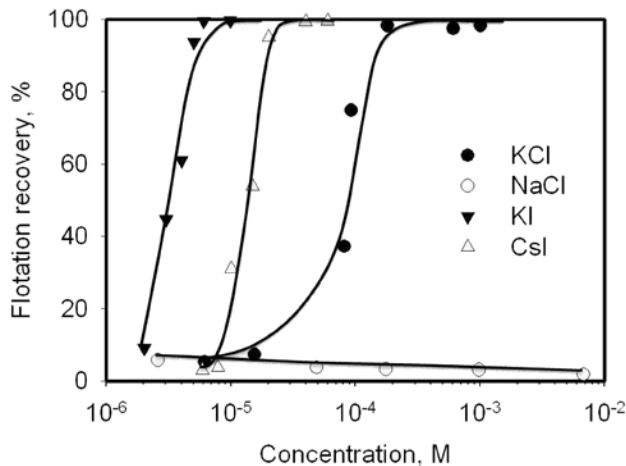
Figure 11 — Flotation of selected alkali halide salts in their saturated brine as a function of DAH concentration (Hancer et al., 2001).
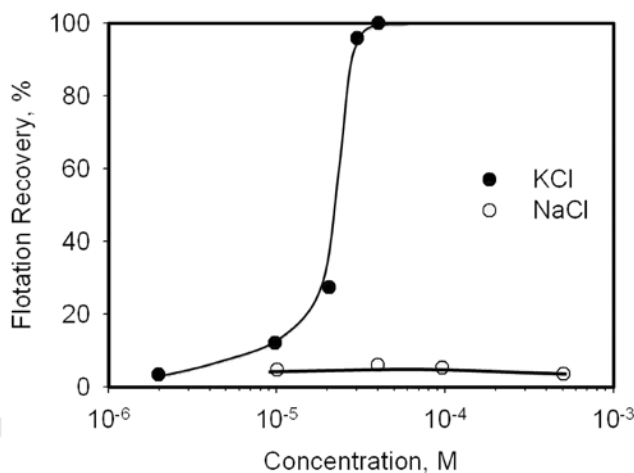

Figure 12 — Flotation of KCl and NaCl in their saturated brine as a function of SDS concentration (Hancer et al., 2001).

reviewed, and important issues deserving further investigation will be discussed.

Alkali halides. Potash is the most important industrial soluble salt, and the great success of KCl recovery via flotation has drawn much research attention for decades. Figure 11 summarizes some of the recent flotation results with respect to selected alkali halide salts in their saturated brines using DAH as the collector (Hancer et al., 2001; Cao et al., 2010). It is evident that KCl, KI and CsI can be very effectively floated using DAH as the collector, and NaCl cannot be floated under the same conditions. Figure 12 illustrates the flotation behavior of KCl and NaCl using SDS as collector and, similarly, good flotation of KCl can be obtained, while NaCl still does not respond well. Therefore, the flotation separation of KCl from NaCl can be realized using either cationic DAH or anionic SDS as collector. Recall from the surface charge analysis that KCl is negatively charged in brine, thus the adsorption of DAH and SDS at the KCl surface is not explained based on the surface charge effect. Hancer et al. and Cao el al. (Hancer et al., 2001; Cao et al., 2010) have proposed that the selective flotation separation of KCl from NaCl can be explained due to the differences in interfacial water structure. KCl is a structure
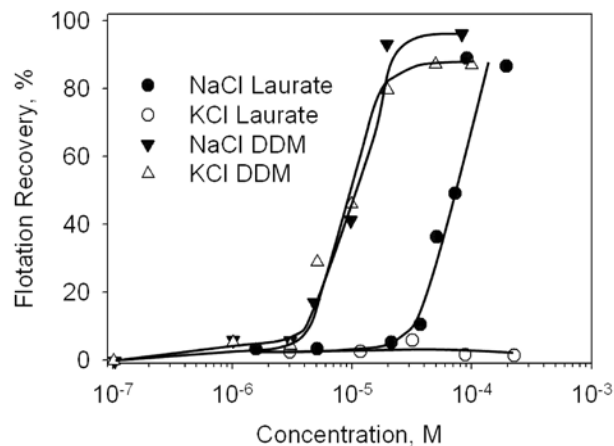

Figure 13 — Flotation of KCl and NaCl in their saturated brine as a function of sodium laurate and DDM (sodecyl amorpholine) concentration (Miller et al., 1992; Hancer et al., 2001).

breaking salt, and the interaction between the surface ions with water molecules is not strong enough to prevent the penetration of collector groups, making it possible for collectors to be adsorbed. In contrast, the structure making salt NaCl has stronger affinity to water molecules, and a stable interfacial water layer at the NaCl salt surface is established, thus inhibiting the adsorption of collectors.

The interfacial water structure theory, however, does not explain the selective flotation of NaCl from KCl using sodium laurate (Miller et al., 1992) or the flotation of NaCl by dodecylmorpholine (DDM) (Titkov, 2004) (Fig. 13). It is interesting to notice that NaCl, which is a typical water structure maker, can float very well with cationic DDM and anionic sodium laurate collectors. In contrast, KCl does not respond well when using sodium laurate as collector. In this regard, in addition to the interfacial water structure, some other factors such as the collector polar group steric effects and hydration effects may have to be considered in future research. For example, DAH and SDS molecules carry relatively bulky polar groups (sulfate and amine groups) with tetrahedral structures, unfavorable for NaCl/collector interaction due to the presence of stable interfacial water molecules. On the other hand, laurate and morpholine head groups exhibit plane structures, which may favor their attachment to the NaCl salt surface without competing with interfacial water molecules. Such speculations require further investigation.

Alkali oxyanions. The flotation response of alkali oxyanions has been extensively studied by Hancer et al. (Hancer et al., 2001) and some of their findings will be briefly discussed in this section. Figure 14 summarizes the flotation responses of $KClO_4$, K_2SO_4 and KNO_3 with the DAH collector. It is evident that, for DAH, the concentration of collector required to float $KClO_4$, K_2SO_4 and KNO_3 is substantially lower than that required for KCl flotation. The flotation order is $KClO_4$ > K_2SO_4 > KNO_3 > KCl. It should be noted that the flotation behavior of KCl in the presence of DAH seems to be attributed to precipitation of the insoluble collector colloid RNH_3Cl, since flotation starts after precipitation (Hancer et al., 2001).

On the other hand, flotation of $KClO_4$, KNO_3 and K_2SO_4 occurs prior to collector colloid precipitation at DAH concentrations as much as two orders of magnitude lower than that required for precipitation. Light transmission results indicate that for the K_2SO_4, KNO_3 and KCl salts, the amine
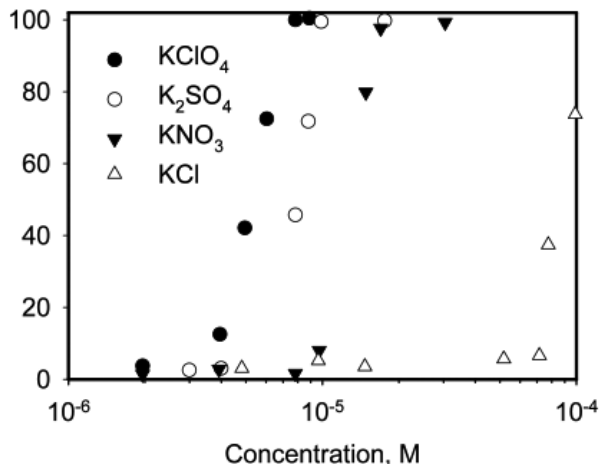
Figure 14 — Flotation of selected potassium oxyanion salts in their saturated brine as a function of DAH concentration (Hancer et al., 2001).
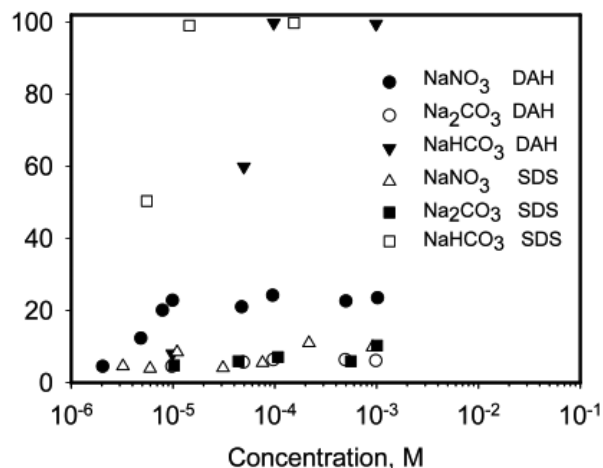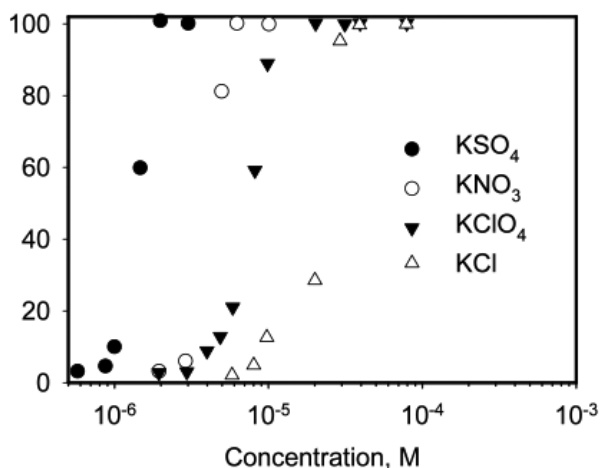

Figure 15 — Flotation of selected potassium oxyanion salts in their saturated brine as a function of SDS concentration (Hancer et al., 2001).

precipitates at a concentration of 1×10^{-4} M DAH, while for $KClO_4$, precipitation of the amine occurs at about 1×10^{-3} M DAH (Hancer et al., 2001). It is evident that formation of the insoluble collector colloid is not required for the flotation of $KClO_4$, K_2SO_4 and KNO_3 using DAH as the collector. The flotation results in the case of DAH can be interpreted in terms of the anions, since all four salts contain the same cation, and selective flotation should depend on the anion as previously suggested by Singewald (Singewald, 1961). On the other hand, this statement does not necessarily mean that only anions are responsible for the flotation behavior of soluble salt minerals. It is evident that cation and anion hydration properties (i.e., charge and ionic radius) can influence the flotation response as exemplified by the results for NaCl and KCl, presented in the alkali halides section.

The order observed in DAH flotation is the same as that observed for the contact angles presented in Table 12, suggesting the significance of interfacial water structures. The large contact angle of brine at the $KClO_4$ surface in the absence of collector (~28°) indicates the weak affinity of the salt to water

Figure 16 — Flotation of selected sodium oxyanion salts in their saturated brine as a function of DAH and SDS concentration (Hancer et al., 2001; Ozdemir et al., 2007; Ozdemir et al., 2009; Ozdemir et al., 2011).

molecules and less hydrated surface states. Consequently, the attachment of collector molecules by replacing the interfacial water molecules is possible. On the other hand, KCl is clearly more hydrated with stronger ion/water interaction, as suggested by the smaller contact angle (~10°); thus, it would take greater energy for the collectors to replace/penetrate the interfacial water and realize adsorption. Under such circumstances, single collector molecules or small collector clusters (micelles) may not be able to bring enough energy to overcome the energy barrier caused by the interfacial water layer, and be selectively adsorbed at the KCl surface; organization of large collector structures such as colloid precipitates/crystals are required to accomplish the task, and air bubbles in the solution may also contribute to facilitate the adsorption processes, which will be discussed further shortly.

With the anionic SDS collector (Fig. 15), it should be noticed that the required SDS concentrations for maximum flotation are lower than those required when DAH was used as the collector (Fig. 14). Generally, it is evident for both DAH and SDS that the flotation order (increasing collector concentration required for flotation) corresponds to the order of increasing structure-making ability. However, a higher concentration of SDS is required for $KClO_4$, probably due to its low solubility of 0.1 M (Hancer et al., 2001). Under these conditions, it is expected that the electrical double layer is not completely compressed and some electrostatic repulsion between the salt surface and collector may still influence the adsorption of the SDS collector. Similar flotation results with DAH and SDS collectors were found for LiF (solubility 0.1 M) (Miller et al., 1992) and for borax (solubility 0.12 M) (Hancer et al., 2001; Celik et al., 2002). Interestingly, KCl and K_2SO_4 saturated salt solutions exhibit precipitation of the SDS collector colloid at a collector concentration of about 2×10^{-5} M. The floatability of these salts is initiated slightly before the onset of SDS collector precipitation. Therefore, the flotation of these negatively charged salts with SDS might be attributed to chemisorption and/or a surface precipitation reaction (Hancer et al., 2001).

The flotation of typical sodium oxyanion salts including $NaNO_3$, Na_2CO_3 and $NaHCO_3$ with regard to collector type (DAH and SDS) were investigated by Hancer et al. and Ozdemir et al., (Hancer et al., 2001; Ozdemir et al., 2007; Ozdemir et

al., 2009; Ozdemir et al., 2011) and their flotation results are summarized in Fig. 16. It is evident that only $NaHCO_3$ exhibits a good flotation response with DAH and SDS as collectors. Recall from previous discussion that $NaHCO_3$ is a structure-breaker salt; therefore, its flotation behavior can be explained on the basis of the unstable interfacial water layer. On the other hand, the structure-making salts $NaNO_3$ and Na_2CO_3 do not respond well with either collector, in accordance with the expectation based on the interfacial water structure theory.

Double salts. Due to the complexity of their composition, soluble double salts have received little research attention, and some of the findings reported by Hancer et al.(Hancer and Miller, 2000) are discussed in this section. The flotation responses of schoenite, kainite and carnallite in the presence of SDS and DAH are shown in Fig. 17. It is clear from the results presented in Fig. 17 that only the schoenite salt is floatable using SDS and DAH collectors. The contact angle measurements (Table 12) have revealed that, in comparison with kainite and carnalllite, which are totally wetted by brine (zero contact angle), schoenite exhibits some degree of hydrophobicity (contact angle 25°). Therefore, the difference in flotation behavior between these salts can be attributed to the difference in surface hydration states, as discussed for alkali halide salts and simple oxyanion salts.

Further, Hancer et al. (Hancer and Miller, 2000) reported that the flotation of schoenite with the anionic collector (SDS) and the cationic collectors (DAH) undergo association with the precipitation of the collector colloids, suggesting that chemisorption and/or chain association followed by surface precipitation may occur at the surface of schoenite but apparently not at the surface of carnallite and kainite.

Effect of pH. The effect of pH in soluble salt flotation systems is of some interest, and previous research has shown that the effect of pH on KCl flotation with dodecylamine is significant (Hancer et al., 2001; Laskowski, 2013). The flotation of KCl and NaCl with dodecyl amine as a function of pH is presented in Fig. 18 (Hancer et al., 2001). It is evident that the flotation of KCl almost ceases beyond about pH 11, while the flotation of NaCl begins to increase at pH 11. The weak electrolyte-type collectors, such as fatty acids and amines, may precipitate, depending on pH, because the solubility limit of free acid or free amine is generally much lower than the corresponding collector salt solubility (Laskowski et al., 2007; Burdukova and Laskowski, 2009; Burdukova et al., 2009; Laskowski, 2013). In the case of amines, precipitation of colloids occurs at high pH with a clear point of zero charge (pzc) at pH 11 (Hancer et al., 2001; Laskowski, 2013). Interestingly, KCl flotation ceases exactly in this pH range, as shown in Fig. 18. This behavior was explained in previous research to be due to the change in the sign of the surface charge of the collector colloid, such that the negatively charged amine colloid and negatively charged KCl could not aggregate under these conditions (pH >11) (Hancer et al., 2001). On the other hand, the flotation behavior of KCl and NaCl can also be explained in terms of the hydrolysis of the collector and/or salt surfaces as suggested by Schubert (Schubert, 1988).

In contrast, the pH insensitivity of KCl and NaCl flotation with SDS (Fig. 19) reinforces the point that the pH dependency associated with amine flotation of KCl and NaCl is due to hydrolysis of the amine collector. SDS is the salt of a strong acid and does not hydrolyze, as is evident from Fig. 19, which shows that KCl and NaCl flotation is not influenced by pH (Hancer et al., 2001). It is shown that changes in pH have no effect on
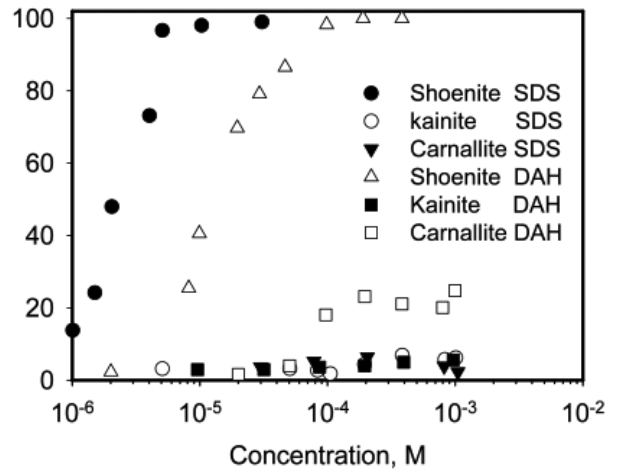

Figure 17 — Flotation response of schoenite, kainite and carnallite as a function of SDS concentration at pH 6.2-7.2 (Hancer and Miller, 2000).
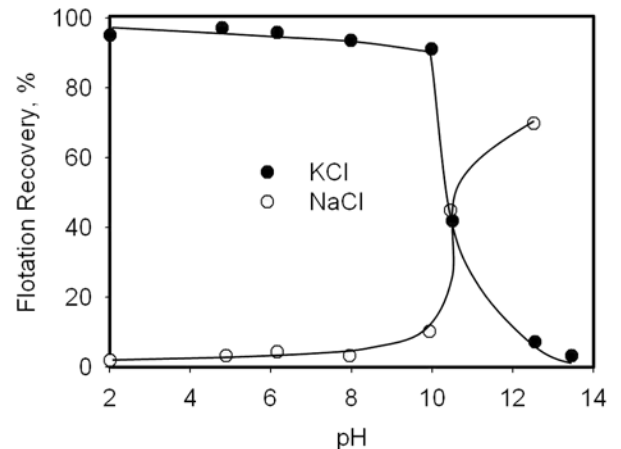

Figure 18 — Effect of pH on flotation recovery of KCl and NaCl with the DAH collector at 3×10^{-4} M (Hancer et al., 2001).
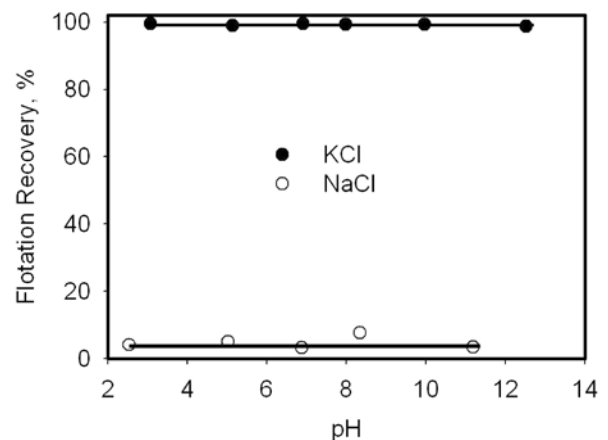

Figure 19 — Effect of pH on the flotation recovery of KCl and NaCl with SDS collector at 1×10^{-4} M (Hancer et al., 2001).
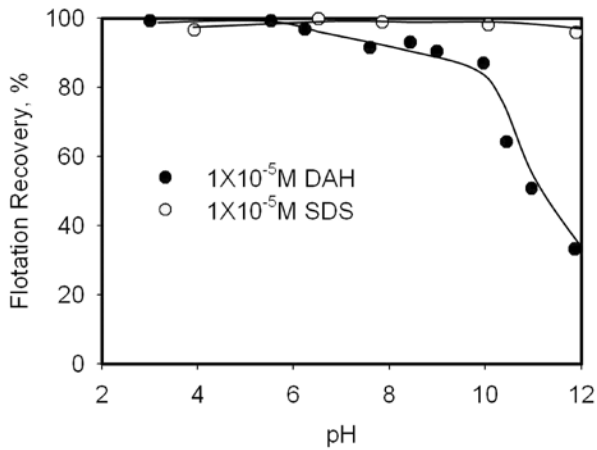
Figure 20 — Effect of pH on the flotation recovery of K_2SO_4 (arcanite) with 1 x 10^{-5} M SDS and DAH (Hancer et al., 2001).
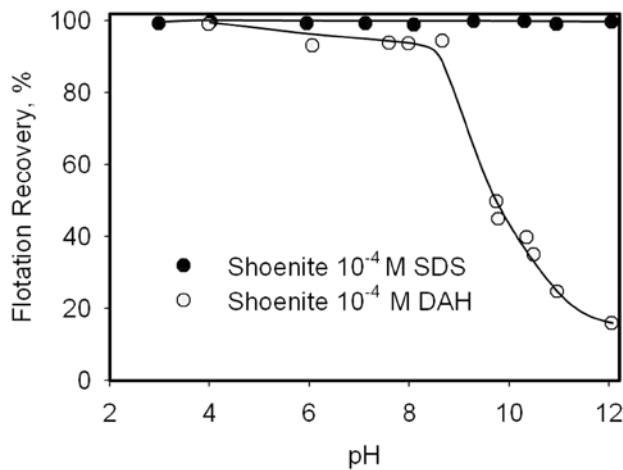

Figure 21 — Effect of pH on the flotation recovery of $K_2SO_4MgSO_46H_2O$ (schoenite) with 1 x 10^{-4} M SDS and DAH (Hancer and Miller, 2000).
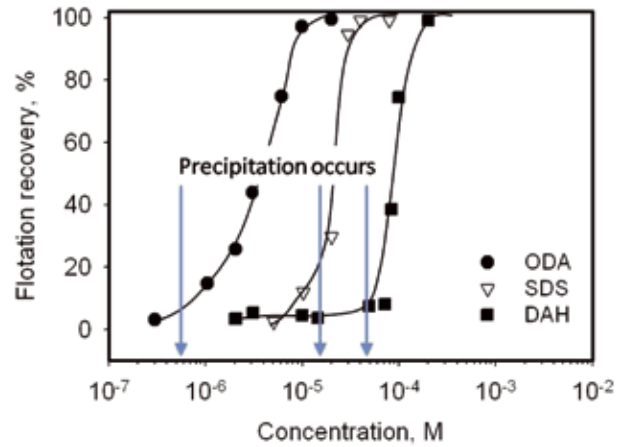

Figure 22 — Flotation response of KCl in this saturated brine as a function of concentration of different collectors (Cao et al., 2010).
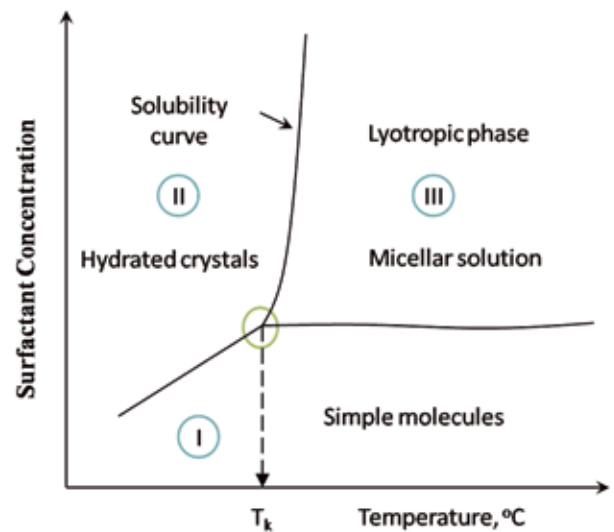

Figure 23 — Schematic representation of the solubility of ionic surfactants versus temperature (Laskowski, 2013).

SDS flotation of negatively charged alkali oxyanions, which will be presented later. It appears from these results that the changes in flotation as a function of pH are in fact very much dependent on the type of collector used.

The flotation of K_2SO_4 (arcanite) and $K_2SO_4MgSO_46H_2O$ (schoenite) as a function of pH with SDS and DAH is presented in Figs. 20 and 21, respectively, and the results are very similar to those observed for KCl (Hancer et al., 2001). As discussed previously, because of amine hydrolysis, K_2SO_4 and $K_2SO_4MgSO_46H_2O$ flotation with DAH decreases above pH 10. These results for K_2SO_4 and $K_2SO_4MgSO_46H_2O$ again clearly show that unlike DAH flotation, pH has no significant effect on SDS flotation due to the fact that the SDS collector is the salt of a relatively strong acid.

Insoluble collectors. The last, but by no means the least, issue that will be addressed in this paper is the phenomenon of collector precipitation associated with the flotation of soluble salt minerals. Practical and experimental results have shown that the flotation of most soluble salts occurs when the solubility limit of the collectors is exceeded (Roman et al., 1968; Schubert, 1988; Miller et al., 1992; Yalamanchili et al., 1993;

Hancer et al., 2001; Titkov, 2004; Schreithofer and Laskowski, 2007; Burdukova et al., 2009; Laskowski, 2013), as suggested by the obvious presence of collector precipitations, which was first observed by Leja et al. (Leja and Schulman, 1954). Figure 22 summarizes the most recent results by Cao et al. (2010) from their study regarding the flotation of KCl. And it is clear that, regardless of collector species, effective flotation of KCl commences when collector precipitation occurs, suggesting that colloid adsorption may be involved in KCl flotation. Schubert (Schubert, 1967) suggested that the crystallization energy of the collector in the brine is of the same order of magnitude as the adsorption energy.

Laskowski et al. (Laskowski et al., 2007; Schreithofer and Laskowski, 2007; Burdukova and Laskowski, 2009; Burdukova et al., 2009; Laskowski, 2013) have systematically examined the significance of collector precipitation with respect to KCl flotation behavior, and have made substantial contributions to the literature. They pointed out that when considering the potash flotation chemistry, the state of the collector in brine has to be considered. Figure 23 illustrates the different phases of collector states in solution. The T_k, Krafft temperature, is the temperature below which the collector colloid cannot be

formed, and hydrated collector crystals exist (Laskowski, 2013). The Krafft points for DAH and ODA were reported to be 26° C and 56° C, respectively (Brandrup, 1975), which dramatically increase with brine concentration. Laskowski et al. further pointed out that, due to the strong salting out effect of saturated brine, the Krafft point of dodecylamine at 16% brine concentration (approximately 1M solution of NaCl-KCl) could be 80° C, and exceed 100° C for ODA (Laskowski, 2013). Thus, all commercial potash ore flotation plants, as well as all lab flotation experiments, were carried out at temperatures much lower than the Krafft temperature of long-chain primary amines and, instead of micelles, precipitates composed of solid particles and hydrated crystals would form in the brines (Laskowski, 2013).

Due to the extreme low solubility of most collector molecules in saturated brine, single molecule diffusion and subsequent adsorption at the salt mineral surface may not occur readily. However, the organization and attachment of the collector could be facilitated via air bubbles, which could be easily covered with a layer of collector, as proposed by Leja et al. (Leja and Schulman, 1954; Leja, 1983) and, later, extensively studied by Laskowski et al. (Schreithofer and Laskowski, 2007; Burdukova and Laskowski, 2009; Burdukova et al., 2009; Laskowski, 2013). The flotation of soluble salt particles can be described according to the following three steps:

1. Formation of collector colloids/crystals once the collector emulsion is added into the brine;

2. Spreading of collector at the air bubble surface once air bubble is introduced into the solution;

3. Attachment of salt particles to collector coated air bubbles.

Summary and conclusions

In this paper, some of the more critical issues with respect to the flotation chemistry of soluble salts have been discussed. It is shown that in order for soluble salts to be floated from saturated brine, numerous factors likely to contribute to the overall phenomenon of selective flotation including crystal lattice, ionic size, hydration of polar groups and salt surfaces, solubility of surfactants and their complexes, surface charge, temperature, etc. should all be considered, as pointed out earlier by Leja (Leja and Schulman, 1954; Leja, 1983). Among all the factors mentioned above, the hydration states of ions and salt surfaces appear to be more significant in governing the collector organization and adsorption at the surface of soluble salt particles in saturated brine.

Ion hydration states analysis suggests that due to the high ionic strength of the soluble salt brine, the water hydrogen bonding network experiences substantial change due to the participation of ion hydration. Water in saturated brine cannot be treated as a continuous phase linked by a hydrogen bonding network. Instead, water molecules become part of the ion hydration shells. Consequently, ions exhibiting different water affinity have different influence on the water hydrogen bonding structure. Small ions such as Li^+ and Na^+ hold water molecules tightly, and immobilize the water molecules in the solution, creating a kosmotropic state of the solution. On the other hand, large ions such as Cs^+ and I^- behave much like uncharged particles in the solution, and form a loose hydration shell, enhancing the mobility of the water molecules. Consequently, a chaotropic state of solution is created. The effect of hydration states of ions on solution properties have been well validated by both viscosity measurements and spectroscopy analysis, and further substantiated by molecular dynamics simulation.

The analysis of ion hydration states has been extended to examine the soluble salt particle interfacial phenomena, and correlated with the flotation responses of different salts. It appears that salts composed of ions with less affinity to water molecules tend to create a more hydrophobic surface as revealed by both contact angle measurements and bubble attachment time measurements. In this way, collector adsorption at such surfaces is facilitated. On the other hand, very stable interfacial water layers will be formed at salts composed of kosmotrope ions, preventing the direct contact of collector molecules with the salt surface.

Exceptions to this water structure theory include the flotation of NaCl with alkyl carboxylates and alkyl morpholine, suggesting that the hydration state of the salt surface is not the only significant factor governing collector adsorption. Collectors can be effectively adsorbed at structure maker salt surfaces equally well as long as the steric effect and the hydration states of the collector polar groups are compatible with the hydration states of the salts. Further research in this area is needed.

The colloid adsorption involved in the soluble salt flotation process is another important issue that deserves extensive study. Considerable evidence suggests that the flotation of soluble salts can only be realized due to the interaction between insoluble collector colloids and salt particles, and such interactions can be promoted via air bubbles in the solution. In this regard, the properties of collector colloids and interaction with salt particles need to be established in more detail in order to advance our understanding of soluble salt flotation chemistry.

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