

The effect of NaCl concentration on the interaction energy between feldspar minerals

Onur Güven ¹, Muhammed Fatih Can ², Cengiz Karagüzel ³

¹ Adana Alparslan Türkeş Science and Technology University, Faculty of Engineering, Department of Mining Engineering, Adana, Turkey

² Afyon Kocatepe University, Faculty of Engineering, Department of Mining Engineering, Afyon, Turkey

³ Dumlupınar University, Faculty of Engineering, Department of Mining Engineering, Kütahya, Turkey

Corresponding author: oguen@atu.edu.tr (Onur Güven)

Abstract: The impact of the usage of monovalent ion concentration on the selective flotation of feldspar minerals has been receiving more attention in recent years. Although many experimental studies have been reported to justify its contribution to their flotation recovery, the effect of particle-particle interaction with theoretical calculations has rarely been studied. The objective of this study was, therefore, to explain the effect of monovalent ion concentration (in particular NaCl) on interactions between albite and microcline particles with a theoretical model based on the classical DLVO. The theoretical modeling results suggested that controlling the monovalent ion concentration not only adjusts the energy barrier between particles but also can be used to determine the critical salt concentration for further tests.

Keywords: DLVO, albite, microcline, NaCl

1. Introduction

Feldspar minerals, Na-feldspar (albite), and K-feldspar (Microcline and orthoclase) have been widely used in many fields such as glass, ceramic, and porcelain industries for a long time (Karaguzel, 2006). Feldspar ores are generally separated from their coloring impurities and quartz by flotation technique (Karaguzel and Cobanoglu, 2010). Although high flotation recoveries can be obtained by optimizing the conditions such as reagent type, concentration, pH, depressant type, etc. (Gao et al., 2018; Ece Kilinc-Aksay, 2018; Gulgonul et al., 2012), the main problem in feldspar flotation is the presence of slimes (usually $-38 \mu\text{m}$ size for feldspar minerals) which adversely affect the flotation by coating the feldspar surfaces due to electrostatic interaction and reducing the flotation recovery (Gulgonul, 1995; Karaguzel, 2010). Accordingly, the flotation efficiency of these fine particles, which exhibit unique characteristics owing to their low mass, impact moments, and high interfacial energy, is very low (Yoon and Luterell, 1989; Tao, 2004; Rodrigues and Rubio, 2007). Therefore, research for explaining the mechanism beyond the separation of fine particles is needed for increasing their recovery by the flotation method. At that point, the interaction degrees between particle-particle and particle-bubble become very important in gathering an idea on optimizing the conditions for a better flotation process (Güven et al, 2022, Yao et al., 2018).

For this aim, the DLVO theory named after the four scientists Boris Derjaguin, Lev Landau, Evert Verwey, and Theodoor Overbeek is used to quantitatively describe the aggregation state of aqueous dispersions through a liquid medium. The theory explains this state by the combination of attractive forces (van der Waals forces) and repulsive forces (electrical double layer forces "EDL") by the effects of the double layer of counter ions. Accordingly, the zeta potential values constitute the major role in these interactions which are used to explain the approaching of particles in an ionic atmosphere, and the development of repulsion force when they overlapped. In addition to these interactions, some additional components such as "hydrophobic" and "hydration" forces are also used in some studies to model the interactions under different conditions when inconsistencies were found between

experimentally measured interactions with theoretical ones (Yoon et al., 1997; Yoon and Vivek, 1998; Pazhianur and Yoon, 2003). These additional interactions then make up "XDLVO" but as this paper will only focus on the calculations and interactions based on classical DLVO theory, the effects of other interactions are planned to be discussed in a future submission along with experimentally measured interactions with AFM (Atomic Force Microscopy). Thus, the interaction energies either calculated or measured with AFM not only show the possible interaction between particles but also give an important insight into their flotation recoveries (Guven et al., 2022; Yao et al., 2018). In other words, following the modeling of the energy barrier between particles, it became possible to determine the suitable condition for its flotation since the first attraction is known to form between particles before adhering to bubbles during flotation (Yao et al., 2018; Yao et al., 2016; Guven et al., 2015).

In this paper, the interactions between albite and microcline were systematically studied by applying classical DLVO theory to inhibit the effect of NaCl concentration on albite and microcline through the energy barrier between particles.

2. Materials and methods

The samples of "Albite" and "Microcline" with high purity used in experimental studies were obtained from the Aydın-Cine region of Turkey. The chemical analysis of the samples (albite: 10.68% Na₂O, 0.42% K₂O; microcline: 11.81% K₂O, 2.84% Na₂O) together with the XRD analysis indicates that the samples are albite, and microcline with albite impurity (Demir et al., 2003). The lump-sized materials were crushed by a hammer and ground in an agate mortar followed by wet screening to produce the sample with -38 µm in size were specially selected for the zeta potential measurements.

2.1. Zeta potential measurements

Zeta potential measurements as a function of electrolyte concentration were conducted with a microprocessor-equipped Zeta-Meter 3.0+ model instrument (Zeta-Meter Inc., USA). All the measurements were carried out under 75 V and the K factor of the measurement cell was 0.71 cm⁻¹. The sample for zeta potential measurements was prepared as follows: about 0.5 g sample was added to 50 ml collector suspension at desired electrolyte concentration and mixed at 360 rpm for 10 minutes to provide suitable conditions for zeta potential measurements. This point is quite important for analysing processes of salt-type minerals because if the suspension has not reached a stable state then the measured values will not present reliable results. This procedure assured the measurements under in-situ conditions. The initial and final pH values of the liquids were recorded for each measurement and the average of at least ten measurements together with their standard deviations for each dispersion was recorded.

3. Results and discussion

3.1. Electro-kinetic measurements

When the zeta-potential measurements vary depending on the ion concentration between albite and microcline, charge changes of two minerals and charge differences between them are observed (Fig. 1). With the addition of NaCl, Cl ions increase the negativity by adsorbing to the mineral surface. The Fig. clearly shows that after 10⁻³ M NaCl concentration, the negativity increases for both albite and orthoclase. This effect is lower in albite than in microcline. With the increase in NaCl concentration, Na ions are replaced by ions in the mineral structure, such as Ca⁺⁺ and Mg⁺⁺, which have higher values. This leads to an increase in the negativity of mineral surface charges. The negativity in albite increases more than the microcline. This is the most basic result explaining selective separation. However, after a certain concentration of NaCl (about 1x10⁻²), the surface charges are directed towards the positive as a result of the suppression of the electrical double layer.

Feldspars, aluminosilicates of sodium and potassium show the same crystal, chemical, and electrophysical properties. Small differences are magnified when the surface of feldspar is substituted by mono and multivalent ions. Feldspar's surface is composed of cationic and anionic centers. While the cations are represented by either Na⁺ in albite and K⁺ in microcline, the anionic centers are the polar silanol groups, i.e.]BSi-OH or relatively non-polar siloxane groups]BSi-O-Si[. Feldspar's surface

charge character is mainly governed by the ratio of the cations and dissociated silanol groups as a function of pH. Increasing the pH leads to an increase in the negative centers and a decrease in pH results in the positively charged centers. The magnitude and sign of the surface potential which determines the extent of adsorption and in turn flotation, are dependent upon the concentration of the constituting monovalent lattice ion, i.e. Na⁺ and K⁺, and the pH of the solution. The floatability of albite and microcline as a function of amine concentration at natural pH exhibited no selectivity between these minerals in the absence of bivalent salts due to close similarities in the physicochemical properties (Demir et al., 2001).

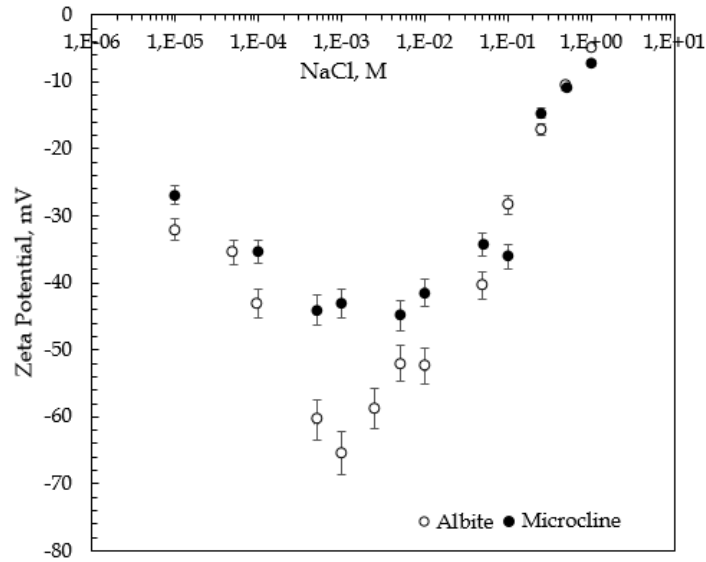


Fig. 1. Zeta potential measurements of albite and microcline as a function of NaCl concentration

3.2. Energy Barrier Calculations

For theoretical analysis, retarded van der Waals, electrical double layer interactions were included for the smooth particle-particle system, allowing for quantifying the energy barrier associated with these interactions for albite and microcline particles. The energy of interactions that combine both retarded van der Waals and electrical double layer contributions (known as DLVO interactions) were calculated according to the model derived earlier. The formulas used for calculating retarded E_{vdw} , E_{EDL} were given in Eqs. 1 and 2.

$$E_{vdw-SPS} = 2\pi RA \left[\frac{-2.45\lambda}{120\pi^2 h^2} + \frac{2.17\lambda^2}{720\pi^3 h^3} - \frac{0.59\lambda^3}{3360\pi^4 h^4} \right] \quad (1)$$

$$E_{EDL-SPS} = 16R(4\pi\epsilon\epsilon_0) \left(\frac{kT}{e} \right)^2 \tanh\left(\frac{e\phi_1}{4kT}\right) \tanh\left(\frac{e\phi_2}{4kT}\right) e^{-\kappa h} \quad (2)$$

where A is the Hamaker constant (J), R is the radius of the particle (m), λ is the characteristic wavelength of van der Waals interactions (m), " h " is the separation distance as measured from the sphere surface, k is the Boltzmann constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$), " e " electronic charge ($1.602 \times 10^{-19} \text{ C}$), T , temperature (298 K), the permittivity of free space ($8.85 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$). The Hamaker constants for albite and microcline samples were taken from the contribution of Lyne et al. 2010 as $8.67 \times 10^{-20} \text{ J}$ and $8.64 \times 10^{-20} \text{ J}$ respectively. Other parameters for retarded van der Waals interactions were adopted from Suresh and Walz. The zeta potential for albite and microcline particles was experimentally determined for each NaCl concentration and shown in Fig. 1. The Debye length of κ^{-1} was calculated for each concentration by using Eq 3.

$$\kappa^{-1} = \left[\frac{N_A e^2}{\epsilon \epsilon_0 k T} \sum_i z_i^2 c_i^\infty \right]^{-1/2} \quad (3)$$

As mentioned in a previous publication the variation in the energy barrier between particles can be caused by the negative surface potentials of interacting surfaces (Drelich and Bowen, 2015). At that point, the energy barrier values for different NaCl concentrations are shown for each mineral in Figs. 2 and 3 respectively.

Fig. 2. shows the changes in total, retarded van der Waals, electrical double layer potentials for varying separation distances between spherical particles.

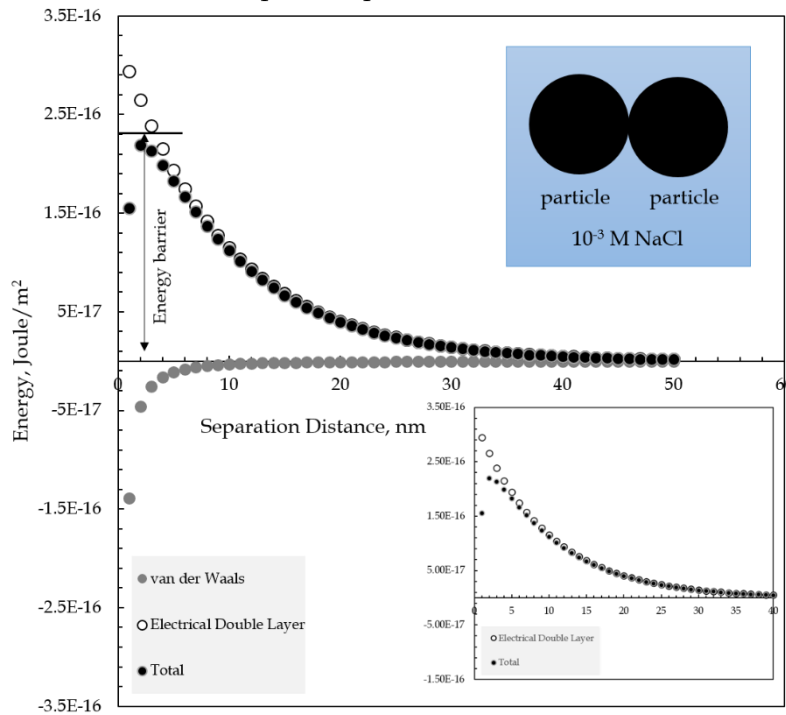


Fig. 2. The interaction energy between 45 μm spherical particles. The total energy is the result of van der Waals and electrical double layer interactions. The following parameters were used: (i) for van der Waals interactions ($A = 8.67 \times 10^{-20} \text{ J}$, $\lambda = 30 \text{ nm}$); (ii) for electrical double layer interactions ($\psi = -65.36 \text{ mV}$, $\kappa^{-1} = 9.6 \text{ nm}$);. Insert at the lower right corner shows “Electrical Double Layer” and “Total Energy” at separations below 40 nm

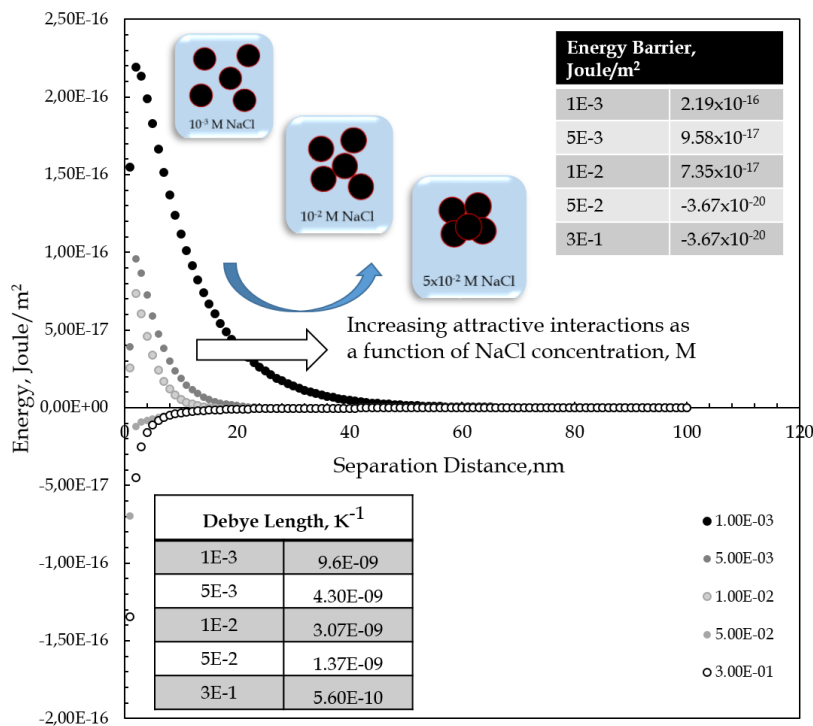


Fig. 3. The interaction energy between 45 μm albite particles. The total energy is the result of van der Waals and electrical double layer interactions as a function of NaCl concentration, M. The following parameters were used: (i) for van der Waals interactions ($A = 8.67 \times 10^{-20} \text{ J}$, $\lambda = 40 \text{ nm}$); (ii) for electrical double layer interactions (the zeta potential values given in Fig. 1 and the Debye Length values given in insert at the lower-left corner)

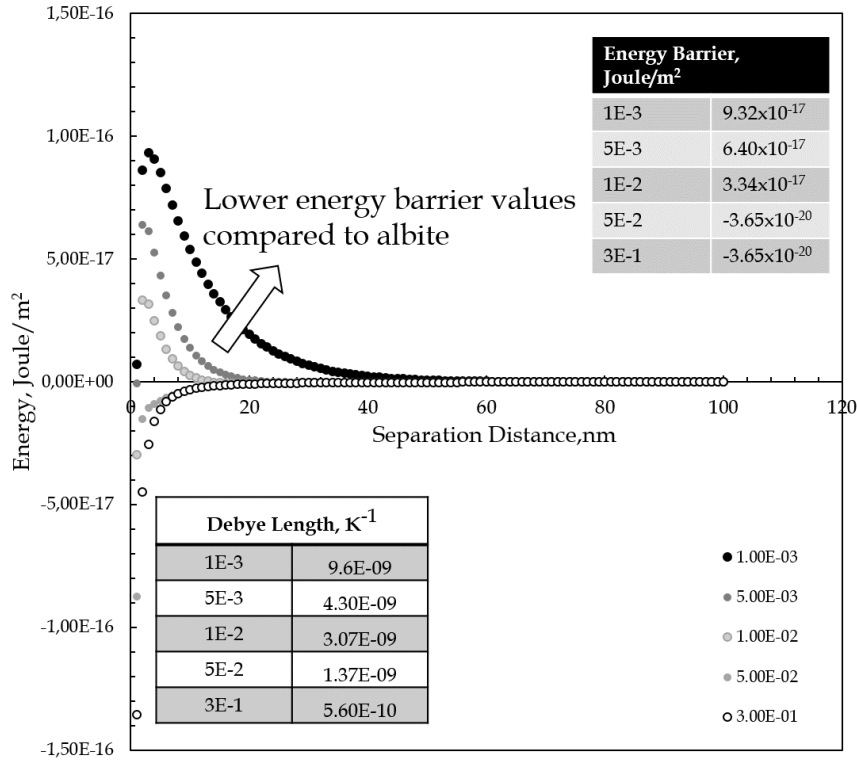


Fig. 4. The interaction energy between 45 μm microcline particles. The total energy is the result of van der Waals and electrical double layer interactions as a function of NaCl concentration, M. The following parameters were used: (i) for van der Waals interactions ($A = 8.64 \times 10^{-20}$ J, $\lambda = 40$ nm); (ii) for electrical double layer interactions (the zeta potential values given in Fig. 1 and the Debye Length values given in insert at the lower-left corner)

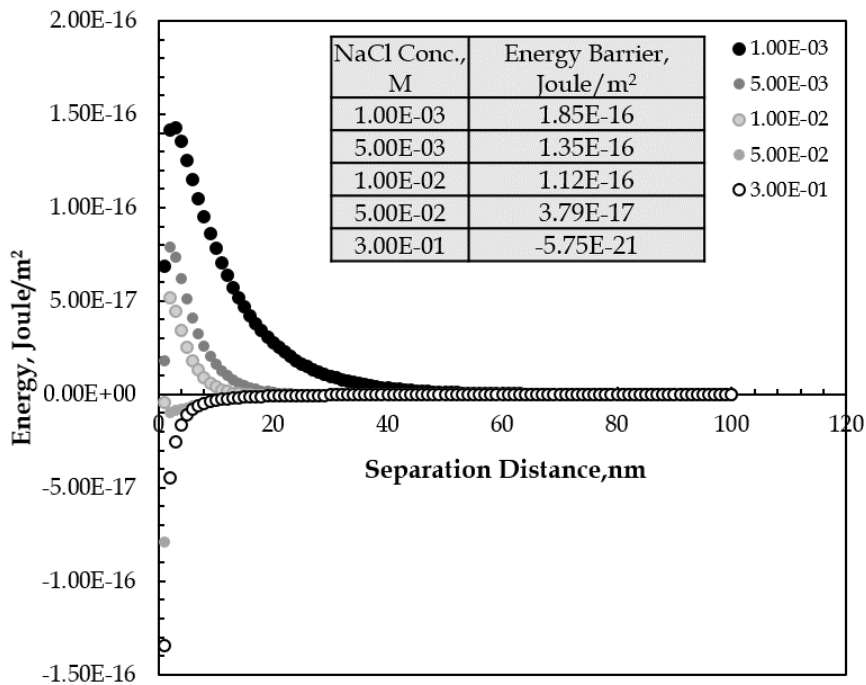


Fig. 5. The interaction energy between 45 μm microcline-albite particles. The total energy is the result of van der Waals and electrical double layer interactions as a function of NaCl concentration, M. The following parameters were used: (i) for van der Waals interactions ($A = 1.36 \times 10^{-20}$ J (calculated by the authors by using the equations and values given in Lyn et al., 2010, $\lambda = 40$ nm); (ii) for electrical double layer interactions (the zeta potential values given in Fig. 1).

As it is previously described, the DLVO model suggests that the interactions are repulsive at a long range before becoming attractive at around 2 nm separation distance at media of NaCl with concentrations up to 10^{-2} M. For this, at around 10^{-2} M concentration, the DLVO model suggests that the interaction should be solely attractive. Within the literature, the experimental data however shows the interactions between the bilayers to be repulsive up until contact. Accordingly, it was assumed that the system is symmetrical and the surface potential ψ is identical for both surfaces. For low zeta potential values, (<60 mV), the Poisson-Boltzmann equation is utilized and it assumes a constant surface potential to describe the forces between charged surfaces with a constant surface-charge regime. Where it represents an increase in the electrical repulsion from the exponential repulsion at small separation. Indifferent concentrations and types of salts were monotonically repulsive up until the bilayers came into contact. The exponential nature of the repulsive interaction reinforcing the dominating role that the EDL forces play in the interactions between cationic bilayers is easily emphasized in the energy/distance plots. As the NaCl concentration increases, the range of the repulsive force decreases, and the interaction becomes weaker. On the other hand, the variation in Debye length is another important parameter to be considered for these calculations. Thus, Debye length values decrease as the salt concentration increases, in agreement with EDL theory. As the electrolyte concentration increases, the number of charged species between the bilayers acts to screen the electrical interaction between the bilayers. This is expressed by the decreasing Debye length, which acts as a measure of the range of EDL interaction. The experimental observations regarding salt concentrations in both zeta pot measurements and flotation Debye length values compare very well to the theoretical values and result in distortions of the outcome over 10^{-2} M concentrations. Decreasing surface potential with increasing electrolyte concentration has been observed for similar surfactant systems and simpler colloidal silica systems (Dishon et. al., 2011; Das et. al., 2013). In simple systems such as silica, it is suggested that increasing the electrolyte concentration increases the surface charge density but decreases the surface and zeta potential. In the surfactant systems, however, the increased electrolyte concentration could also be affecting the local packing within the supported bilayers. (Redondo-Morata et. al., 2014).

Taking into account that knowledge in mind, as can be seen in Figs. 3 and 4, while repulsive interactions dominate the total interactions in low concentrations such as 1×10^{-3} M NaCl, a significant variation was obtained upon increasing the concentration to 5×10^{-2} M for both albite and microcline. In other words, while the energy barrier value was 2.19×10^{-16} Joule/m² at 1×10^{-3} M NaCl concentration for albite and 9.32×10^{-17} for microcline, a very significant decrement to -3.67 Joule/m² and -3.65×10^{-20} Joule/m² for both minerals were calculated for 3×10^{-1} M NaCl. And as shown in the table given in the insert at the upper-right corners of the Figs., the energy value was the same over 5×10^{-2} M NaCl concentration for both of them. On the other hand, if the interactions between albite and microcline are considered for modeling the possible interaction between different feldspar minerals (Fig. 5), similar trends were obtained for lower salt concentrations than 5×10^{-2} M, the attractive forces dominate the system over that concentration.

However, it is worth noting that below that concentration, considerable differences were obtained for each mineral. This can be ascribed to the structural differences between albite and microcline particles also varied the ion exchange characteristics which in turn resulted in different zeta potential values under the same salt concentration. Thus, regarding their close Hamaker constant values and the values of other parameters such as particle diameter, debye length, Poisson Boltzmann constant values, etc., the zeta potential values are the main parameters to adjust the energy barrier between particles. In addition, following that critical concentration, the dominancy of repulsive interactions became lesser and the attractive interactions come into the front for total interaction between particles. Therefore, as shown in the schematic picture in the upper-left corner of Fig. 3, the aggregation of particles may form with an increasing salt concentration in the system. Concerning that increasing particle-particle interaction, so to say possible agglomeration of fine particles, a similar trend can be suggested for bubble-particle interactions which in turn higher flotation recoveries. In literature, the effect of salt concentration within the presence of a cationic collector as G-TAP was reported for the flotation of both albite and microcline (Karaguzel et al., 2005, Demir et al., 2003). Their results showed that an almost 70 % difference could be obtained by the addition of NaCl within the presence of 0.3 mg/L G-Tap in the

system. Although the presence of a reagent even at a low concentration can change all characteristics of mineral surfaces, the effects of salt concentration in percent (Demir et al., 2003) can be used to prove the findings of the energy barrier calculations for different salt concentrations.

These findings, in our opinion, indirectly explain the results of micro-flotation discussed in the previous reports since the same cation was investigated in this study in terms of its effect on the particle-particle interaction. Thus, the findings of this research further suggest that the modeling of particle-bubble interactions in the presence of monovalent salts would present a better explanation of flotation results and lead to improvements in flotation separation.

4. Conclusions

To explain differences in particle-particle interactions of albite and microcline particles with smooth surfaces, a theoretical model on DLVO interaction energy was adopted for this research. The calculated energy barrier under different NaCl concentrations showed that while the repulsive interactions dominate the total forces in a wide range of concentrations, the attractive forces became dominant upon a critical concentration for both minerals. These findings showed that adjusting the salt concentration in suspension will lead to the aggregation of particles.

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