Zeta potential of Teflon in presence of monovalent and divalent ions

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Abstract: In this study, the specific effects of Na^+ and Ca^{2+} ions on natural hydrophobic Teflon particles and flat Teflon surfaces were investigated using zeta potential and contact angle measurements, respectively. The zeta potential measurements showed that the surface charge of Teflon was negative at all pH values in the absence of salt ions, and became the positive with the increased salt concentration, and obtained an iso electric point (iep) between pH 3 and 4. The results also indicated that Ca^{+2} ions more adsorbed on the Teflon surface compared to Na^+ ions in the case of the compression of the electrical double layer. The contact angle measurements with Teflon sample showed that while the flat Teflon had a contact angle of 107° at pure water, and the contact angle considerably reduced as a function of salt concentration. This decrease was more effective in the presence of Ca^{2+} ions rather than Na^+ ions. While calcium is a strong water structure maker cation, sodium is a weak structure maker cation, but the role of calcium is more effective at the Teflon-water interface according to zeta potential and contact angle measurements. It is revealed that the Ca^{+2} ions have a specific effect on Teflon surface due to low salt concentrations and ion charges. The different effects of these cations on Teflon-water interface can be attributed to use in mineral processing, especially in flotation enrichment.

1. Introduction

Polytetrafluoroethylene (Teflon-PTFE) has a molecular structure consisting of a long and flat carbon chain, chemical name is tetrafluoroethylene (TFE), saturated with fluorine atoms. Teflon has high physical and chemical properties due to strong bond formation between carbon and fluorine atoms. For example, Teflon is insoluble in any solvent, acid or base, and when melted, it forms a flowless (non-flowing) stiff clear gel (Ebnesajjad, 2016). Teflon colloids have a high surface area and defined shape compared to other hydrophobic surfaces such as inert gases (bubbles), hydro carbon oils (droplets), ice (melts at temperatures higher than 0°C) or diamonds (expensive) (Preocanin et al., 2012). PTFE dispersions are aqueous milky dispersions consisting of very small particles (<0.25 mm) of resin suspended in water. This form of PTFE is about (96-98%) crystalline, and contains non-ionic surfactant, which to stabilization of dispersion also promote the wetting of the substrate (Ebnesajjad, 2014).

Moreover, Teflon does not adhere to any substance, and its contact angle in water is above 90° due to its very high hydrophobic property (Drelich et al., 1996; Kowalczuk and Drzymala, 2011; Kosior et al., 2013; Kowalczuk and Zawala, 2016). In flotation applications, PTFE particles remain in the liquid/gas interface for a very short time like 5 sec (Kowalczuk, et al., 2016), meaning that PTFE can be easily recovered by flotation in pure water without surfactant (Kowalczuk and Zawala, 2016). The most basic properties of Teflon are low dielectric constant, high thermal resistance, a low coefficient of friction, low flammability, and use in broad temperature, resistance to UV rays, hydrophobicity, oleophobicity, and chemical inertness. Because of these characteristics of Teflon, it is used in a wide range of products in industry, especially medical, electronics, defense, computer, telecommunication, and fabric products (Ebnesajjad, 2016). Compared to other materials such as glass and silicone, Teflon has mechanical, electroosmotic properties as well as low cost and simplified production procedures.

Many polymetric substrates such as Teflon are less well known than silica or silicon due to the difficulty in accurately and precisely measuring the zeta potential properties. While silica surfaces generally have high bulk density and hydrophilic surfaces, polymers such as Teflon have hydrophobic surfaces and very low zeta potential profiling, influenced by welds or manufacturing methods whose surface charge is generally unknown (Kirby and Hasselbrink Jr, 2004).

Teflon particles, which are natural hydrophobic in aqueous suspensions, can be separated easily from hydrophilic particles by foam flotation. In addition, when Teflon particles are vigorously agitated and continuous fine air bubbles are given; stable agglomerates are formed, and easily separated from hydrophilic particles by means of foam flotation. In this study, zeta potential and contact angle measurements were carried out to determine the surface properties of the natural hydrophobic Teflon particles in the absence and presence of Na^+ and Ca^{2+} ions, and most importantly the interactions at the Teflon-water interface layer.

2. Materials and methods

2.1. Materials

In this study, two Teflon samples (plate and powder) obtained from Polikim and Apameya companies in Gebze-Turkey were used in the experiments. The average particle size of the sample was 6-8 μm as specified by the suppliers. The plate Teflon sample was cut to size 20×20×5 mm used for the contact angle measurements. The samples were firstly washed with water and then ethyl alcohol, and dried in the desiccator at the room temperature (23±1ᵒC). With 99% purity of salts of sodium (NaCl) and calcium (CaCl₂) used in this study were purchased from Aldrich-Chemie and Fluka-Chemie, respectively. Ultra-pure water was used for the experiments (Milli-Q Elix&Simplicity 185 purification system, Millipore SA Molsheim, France). The acidity was adjusted by adding either HCl (37-38%, Merck) or NaOH (98% purity, Erba).

2.2. Methods

2.2.1. Zeta potential experiments

Streaming potential of a polytetrafluoroethylene (PTFE) surface was determined in the plane-parallel electrokinetic cell of the home-made apparatus described in literature (Zembala and Adamczyk, 2000; Zembala, 2004; Adamczyk et al., 2010), and illustrated schematically in Fig. 1.

The cell constitutes the main part of the apparatus and consists of two polished Teflon blocks. One of the blocks contains two rectangular inlet and outlet compartments. Between the Teflon blocks, two PTFE sheets are placed, separated by a Teflon gasket of the thickness of 0.025 cm serving as the spacer. The parallel plate channel of dimensions: $2b$ = 0.025 cm x $2c$ = 0.33 cm x L = 6 cm, is formed by clamping together the Teflon blocks with two PTFE sheets and the spacer between them. All parts are clamped with a press under constant torque conditions (Zembala and Adamczyk, 2000) to avoid the distortion of the channel, and to keep the constant channel dimensions. The whole set-up is placed in the grounded Faraday cage to avoid any disturbances stemming from external electric fields.

The streaming potential, E_s, is measured using a pair of Ag/AgCl electrodes as a function of the hydrostatic pressure difference, ΔP_s, which is driven by the electrolyte flow through the channel. Moreover, the overall cell electric conductivity, K_e, is determined using a pair of Pt electrodes. Knowing the slope of the E_s vs. ΔP_s, the apparent zeta potential of a PTFE substrate (ζ_i) is calculated from the Smoluchowski's relationship:

$$\zeta_i = -\frac{\eta L}{4\varepsilon b_c c_c R_e} = -\frac{\eta K_e}{\varepsilon}\frac{\Delta E_s}{\Delta P_c} \tag{1}$$

where η is the dynamic viscosity of the solution, ε is the dielectric permittivity, R_e is the electric resistance of the cell governed mainly by the specific conductivity of the electrolyte in the cell, and K_e is the specific conductivity of the cell, connected with the electric resistance via constitutive relationship:

$$R_e = \frac{L}{\Delta S_c K_e} = \frac{L}{\Delta S_c \left(K_e + K_s^{'}\right)} \tag{2}$$

where ΔS_c is the channel cross-section area, K_e is the specific conductivity due to electrolyte, and K'_s is the surface conductivity depending (in the generally) on the channel shape. The correction for the surface contribution is introduced in a standard way, previously described in literature (Zembala, 2004). The correction is ca. 10% for ionic strength of 1.10^{-4} mol/dm³, and practically negligible for higher ionic strength.
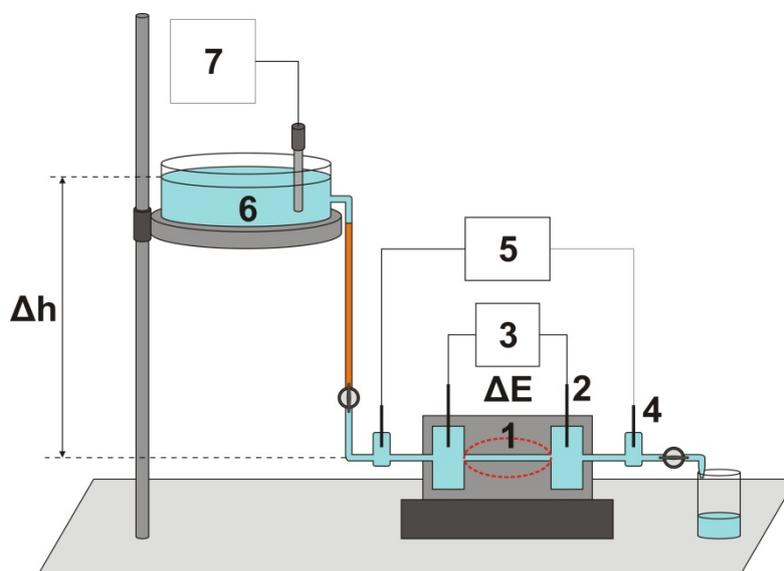
Fig. 1. A schematic view of the parallel-plate channel cell used for streaming potential measurements of bare surfaces of PTFE: 1) electrokinetic cell; 2) AgCl electrodes for streaming potential measurements; 3) streaming potential measurement set-up (electrometer); 4) electrodes for cell resistance measurements; 5) resistance measurement set-up (electrometer and resistor) 6) electrolyte reservoir 7) conductometer (Morga et al., 2016)

Using this technique, experiments are usually performed under well-controlled hydrodynamic laminar conditions, in a channel or capillary with a large radius compared to the double layer thickness. The streaming current results from the convective flux of ions from the thin double-layer region adjacent to solid/electrolyte interfaces. This streaming current is provoked by a macroscopic flow of the fluid, usually driven by the hydrostatic pressure gradient (e.g. channel and capillary flows). As a result of charge separation caused by the flow, an electrostatic potential difference appears along the interface, proportional to the streaming current, which is called the streaming potential.

For the purpose of PTFE surface characterization, the procedure of performing streaming potential measurements was as follows:

i)   A reference measurement of the streaming potential of a PTFE surface in a pure electrolyte of I = 10^{-2} mol/dm³ and naturally occurring pH was performed.
ii) The channel was then filled with an electrolyte of a proper ionic strength, and the streaming potential measurement was conducted under the same pH conditions.
iii) For electrolytes of lower ionic strengths (10^{-3} mol/dm³) the corrections connected with the electric resistance was evaluated.
iv) Furtherly, the channel was filled with an electrolyte under naturally pH and the streaming potential measurement was repeated.
v)   Next, the pH dependence was carried out for each kind of electrolyte and fixed ionic strength starting from pH 5.6 and examined towards basic conditions.
vi) Then, the backward cycle was performed from basic pH towards pH 5.6.
vii) Afterwards, the PTFE sheets were taken out from the cell, cleaned with water and ethanol and put back into the electrokinetic cell.
viii) The streaming potential measurements were performed starting from naturally occurring pH and examined towards acidic conditions.
ix) The measurements were performed separately for each type of the electrolyte.

2.2.2. Contact angle measurements

The contact angle measurements for Teflon samples were carried out using an optical tensiometer (Biolin KSV, Sweden). The Teflon samples about 20×20×5 mm sizes were used for the contact angle measurements. Sessile drop method was used in the measurements, and water droplet formation was manually performed using a 1 cm^3 glass syringe (Dynatech Precision Sampling, USA). The volumes of water droplets formed in the measurements were kept in a volume range of 3-5 μL, and measurements were taken from 10 different points of the surfaces.

3. Results and discussion

3.1. Zeta potential measurements

Since the use of salt ions in industry is inevitable in aqueous solutions, adsorption of these salt ions to surfaces of natural substrates such as Teflon will directly affect their surface charges. However, in literature, the surface charge of hydrophobic surfaces in contact with water is controversial about positive or negative, and is not fully resolved (Beattie, 2006; Kudin and Car, 2008; Winter et al., 2009a, 2009b; Gray-Weale, 2009; Ehre et al., 2010; Preocanin et al., 2012). The electrokinetic measurements of natural hydrophobic substrates are difficult (challenging) because of their noteworthy scattering in the data obtained (Kirby and Hasselbrink Jr, 2004), and also are sensitive to surfactants (Tandon et al., 2008). There is no forceful theory describing the interactions between electrolyte solutions and naturally uncharged air, oil and hydrophobic solid phases (Welzel et al., 2002). For this purpose, systematic zeta potential measurements were performed in order to examine the contribution of Na^+ and Ca^{2+} ions at the hydrophobic Teflon surfaces. Fig. 2 and Fig. 3 show the zeta potential-pH profiles of Teflon sample as a function of NaCl and CaCl$_2$ concentration (1.10^{-3} mol/dm^3, 1.10^{-2} mol/dm^3, and 0.15 mol/dm^3), respectively. As seen from Figs. 2 and 3, Teflon has a negative surface charge at neutral and all alkali pH's in both NaCl and CaCl$_2$. As the pH of the medium goes from neutral to acidic, the surface charge of Teflon rapidly approaches the positive, and has an iso electric point in the range of pH 3-3.5. For Teflon, detected of the iso electric point and the measured zeta potential measurement results are consistent with the results in literature (Welzel et al., 2002; Kirby and Hasselbrink Jr, 2004; Beattie, 2006; Preocanin et al., 2012; Ebnesajjad, 2016). Nonetheless, many recent research studies have shown that Teflon, a natural hydrophobic material, has a generally negative surface charge at neutral and alkali pH's, and shows isoelectric points between pH 2 and pH 4 (Welzel et al., 2002; Kirby and Hasselbrink Jr, 2004; Beattie, 2006; Preocanin et al., 2012; Ebnesajjad, 2016). As there are no reactive surface groups, polymers such as Teflon are chemically inert. At the neutral pH (pH 7), the chemical source of the Teflon's surface charge being negative, and its low pH dependence has recently been described as 'yet unclear' (Kirby and Hasselbrink Jr, 2004; Beattie, 2006).

In the zeta potential-pH profile of Teflon, whereas the values of the adsorption of hydroxide ions are more dominant at the neutral and alkaline pHs, hydronium ions appear to be more adsorbed on the interface at the values below pH 4 (Zimmermann et al., 2001; Zimmermann et al., 2009). The main reason for the low iso electric point of Teflon can be explained as the preferential adsorption of hydroxyl ions compared to hydronium ions (Welzel et al., 2002). Soster et al. (2005) claimed that the negatively charged hydroxyl ions better adsorbed to the clean PTFE surface, and hence increased negativity. As a result, in Teflon / water systems, it appears that the hydroxide ions preferably absorbed at the solid-water interface, and cause a net negative surface charge. When the pH is lowered, the protons neutralize this negative surface charge, causing an isoelectric point around pH 4. From the iso electrical point, that is in acidic regions (pH> 3-4), the surface charge of Teflon has positive values. Although most hydrophobic polymers, such as Teflon, do not have reactive surface groups and a strong affinity for ions, they have a similar electrokinetic potential profile as charged hydrophilic surfaces such as glass (Tandon et al., 2008).

In Figs. 2 and 3, as the amount of salt ion increases in the solution, the surface charge of Teflon approaches towards the positive and it appears to be greater in the presence of Ca^{2+} than in the presence of Na^+ ion. For example, at pH 7.2, while the Teflon has a -57 mV surface charge in the presence of 1.10^{-3} mol/dm^3 NaCl, the surface charge increases to -40 mV at the 1.10^{-2} mol/dm^3 and -22mV at the 0.15 mol/dm^3 NaCl (Fig 2). In the presence of CaCl$_2$ at about pH 7.2, the surface charge of Teflon is -40

mV at the 1.10^{-3} mol/dm³, it increases to -31 mV at 1.10^{-2} mol/dm³ CaCl$_2$ and then -16 mV at the 0.15 mol/dm³ CaCl$_2$ (Fig. 3). When the salt ions are added to aqueous solutions, since these ions absorb specifically at the solid-liquid interface, they will directly change the zeta potential by affecting the surface charge. If some ions preferably adsorbed on others due to differences in affinity or hydration energy, these salt ions caused in a net surface charge density in buffered solutions (Lyklema, 1991; Israelachvili, 1992). Although hydroxyl ions tend to be more hydrated than hydronium or salt ions (Israelachvili, 1992), it is believed that they preferably adsorbed onto aqueous-hydrophobic interfaces resulting in a net negative surface charge density (Beattie, 2006). Since the inert hydrophobic materials do not have active surface areas, the electrical interfacial layer can be said to be formed by the sequencing of water molecules and by other ions around the surface (Beattie, 2006; Tandon et al., 2008; Lutzenkirchen et al., 2008; Preocanin et al., 2012).
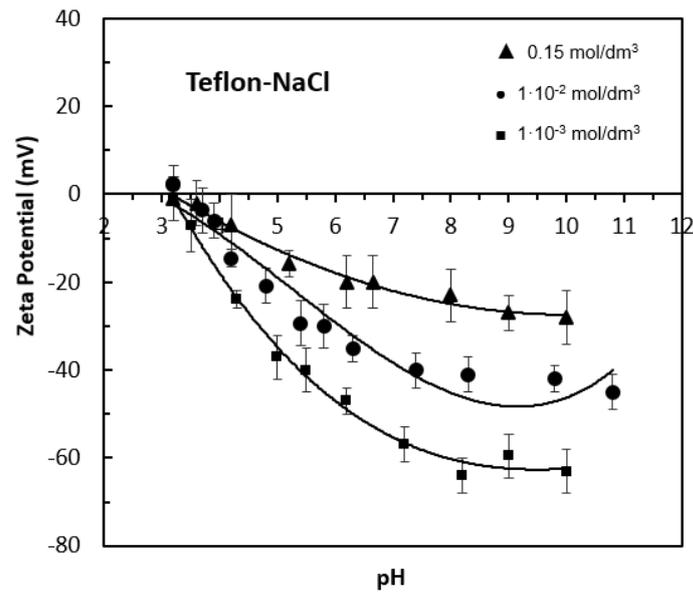
Fig. 2. Zeta potential-pH profiles of Teflon as a function of NaCl concentration (1.10^{-3} mol/dm³, 1.10^{-2} mol/dm³, and 0.15 mol/dm³)
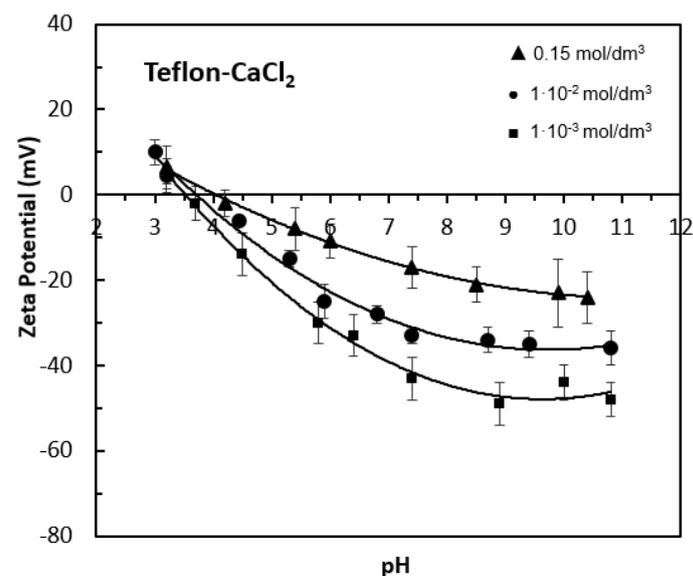
Fig. 3. Zeta potential-pH profiles of Teflon as a function of CaCl$_2$ concentration (1.10^{-3} mol/dm³, 1.10^{-2} mol/dm³, and 0.15 mol/dm³)

In order to better analyze the effects of Ca^{2+} and Na^+ ions on the Teflon surface charge, the zeta potential curves were drawn based on pH at constant salt concentrations (1.10^{-3} mol/dm³, 1.10^{-2} mol/dm³, and 0.15 mol/dm³), and shown in Figs. 4, 5, and 6, respectively. While at constant 1.10^{-3} mol/dm³ NaCl concentration in Fig 4, the surface charge of Teflon was -63 mV at the pH 10, it increased to -57 mV at pH 7.2, and -1 mV at pH 3.2. In the presence of 1.10^{-3} mol/dm³ $CaCl_2$, surface charge increased from -47.5 mV at pH 10 to -43 mV at pH 7.4 and +4.6 mV at pH 3.2, respectively. Ca^{2+} ions caused neutral (zero) the surface charge of Teflon (iso electric point) at the pH of about 3.5. It can be concluded from these results that calcium ions are more preferentially adsorbed than sodium ions at the interfaces (Zimmermann et al., 2009). Therefore, considering the compression of the electrical double layer, it is clear that Ca^{2+} ions were more effective than Na^+ ions. It also appears that the adsorption of the chloride ion competing with the hydroxide ion in the solution does not have any effect on the reduction of the zeta potential (Marinova et al., 1996; Beattie, 2006). Related to this issue, Zimmermann et. al. (2001) measured the zeta potential of the Teflon AF film as -120 mV of at pH 9 in the presence of 0.1 mol/dm³ KCl, and an iso electric point of Teflon was pH 4. They also claimed that chloride ions had no effect on the negative surface charge.

In Fig. 4, the type ($NaCl$-$CaCl_2$) or presence of salt electrolyte affected the zeta potential of Teflon more than the iso electric point region in the neutral and alkaline pH range. However, with the increase of hydronium ions (pH>5), the difference between the effect of Ca^{2+} and Na^+ ions decreased, and the zeta potential curves approached each other. At pH values below iso electric point, besides very little changes in surface charge, the interactions between Ca^{2+} and Na^+ ions on the hydrophobic Teflon surface were also very small. Therefore, it may be concluded that electrokinetic measurements to distinguish these interactions cannot be sensitive due to increased ionic strength (Zimmermann et al., 2009). By increasing the salt concentrations, 1.10^{-2} mol/dm³ (Fig. 5) and 0.15 mol/dm³ (Fig. 6), the difference between the effects of Ca^{2+} and Na^+ ions on the Teflon surface charge further reduced, and zeta potential curves approached each other. Especially on 0.15 mol/dm³ salt concentrations in all pH zones, the differences between the Teflon surface charge measurements were constant, and measured very close to each other in Fig. 6. Of course, the increase of hydronium ions in the medium (pH> 5) means that water ions may be dominant in the charging of Teflon / electrolyte interfaces (Welzel et al., 2002). With the increase of ionic strength, the zeta potential decreases by compression of the electrical double layer or an increasing part of the surface charge is balanced in the hydrodynamic immobile layer at higher ionic strength (Zimmermann et al., 2009).
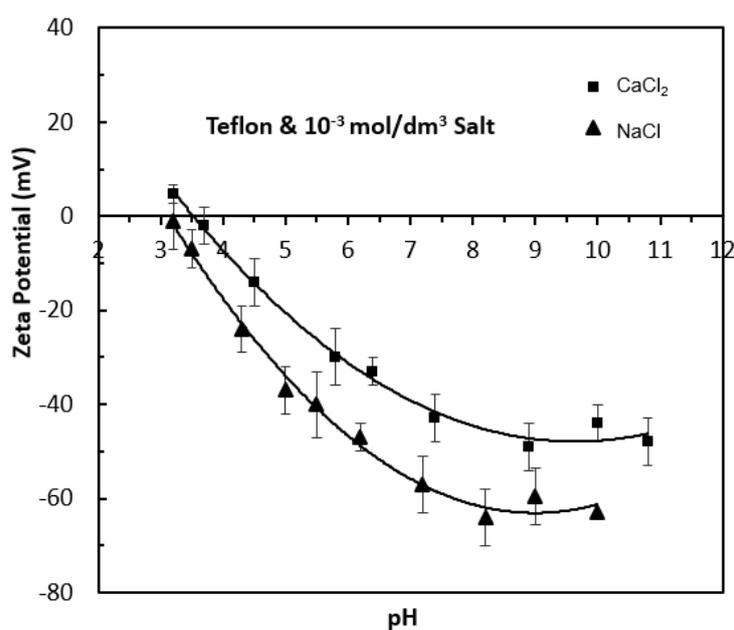
Fig. 4. Zeta potential-pH profiles of Teflon at 1.10^{-3} mol/dm³ $CaCl_2$ and NaCl solutions
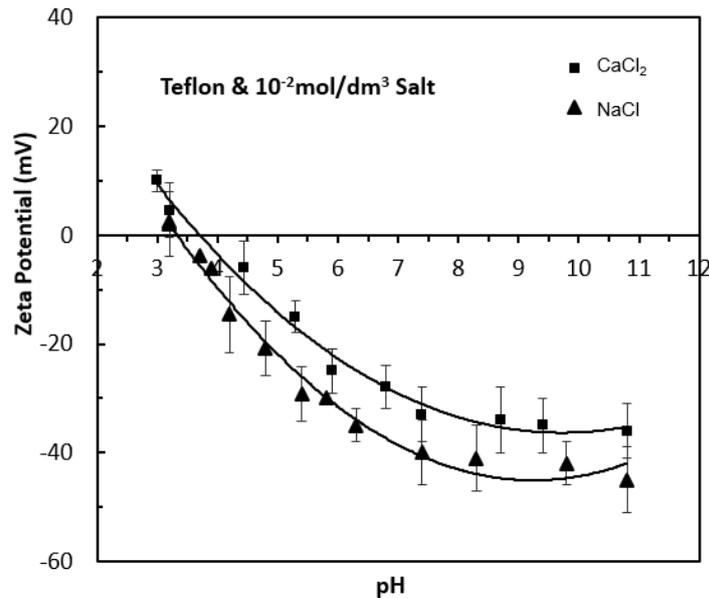
Fig. 5. Zeta potential-pH profiles of Teflon at 1.10^{-2} mol/dm^3 CaCl$_2$ and NaCl solutions
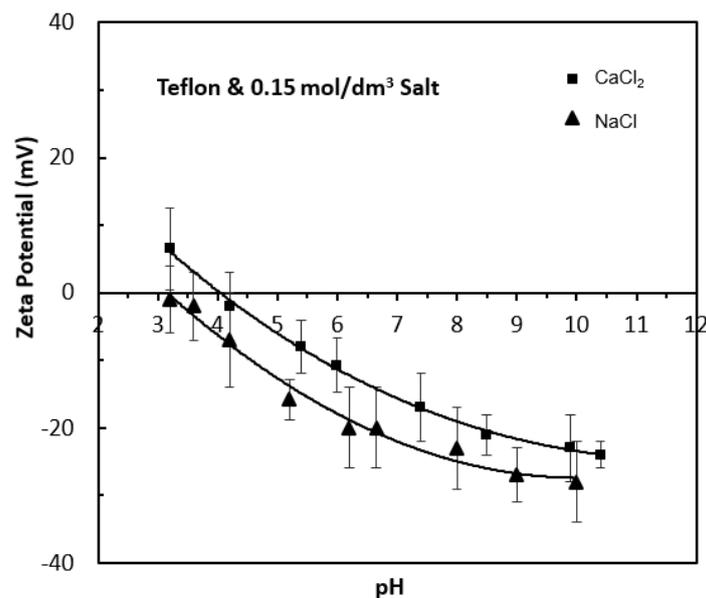
Fig. 6. Zeta potential-pH profiles of Teflon at 0.15 mol/dm^3 CaCl$_2$ and NaCl solutions

3.2. Contact angle measurements

The most common parameter used to define the wettability of a solid in liquids is the contact angle. It is therefore important to understand and characterize the wettability of the solid surfaces. Due to the low surface energy of hydrophobic solid surfaces such as Teflon, the wettability in aqueous solutions is difficult to do properly. While the free surface energy of Teflon is 18-20 mN/m (Kinloch, 1987; Goss, 2010; Ebnesajjad, 2014), the surface tension of the water is 72.8 mN/m, and it has a direct hydrophobic property. Furthermore, in order to increase the wettability of the solids in water or to reduce the free surface energy of the media, surfactants must be added. In literature, the effect of surfactants on the contact angle and wetting is very clear (Eckmann et al., 2001; Zdziennicka et al., 2003; Chaudhuri and Paria, 2009), as well as in the presence of electrolytes (Morton III et al., 2008; Chaudhuri and Paria, 2009). In this purpose, the contact angles of the pure Teflon samples were measured as a function of sodium

and calcium ions, and the results are seen in Fig. 7. The contact angle of the flat Teflon was found to be 107° in the pure water in which is full agreement with literature (Janczuk et al., 1985; Spagnolo et al., 1996).

An iso electric charge point for the Teflon sample was found at approximately pH 3-3.5 in the presence of NaCl and CaCl$_2$ from the zeta potential measurements. The Teflon surface is negatively charged above this pH and positively charged below. By the addition of salt to the medium, the compression of the electrical double layer or the effectiveness of the hydronium (H$_3$O$^+$) ions (Marinova et al., 1996; Eckmann et al., 2001; Zimmermann et al., 2001, 2009; Welzel et al., 2002; Soster et al., 2005) were reduced both the zeta potential (Fig. 2-Fig. 6) and the contact angles (Fig. 7). In addition, when the Teflon surface is loaded, in other words, when Na$^+$ or Ca^{2+} ions are added into the medium, the interaction with water will be more effective (Zimmermann et al., 2009; Welzel et al., 2002), and therefore the contact angles will decrease as shown in Fig. 7. According to the zeta potential measurements; due to the fact that Ca^{2+} ions more adsorbed than Na$^+$ ions at the interface (Zimmermann et al., 2009), the results in Fig. 7 are also shown that CaCl$_2$ reduces the contact angle more effectively than NaCl.

It should be mentioned that the variation of interfacial water structure with salt type (Ozdemir et al., 2007), structure making salts cause the surface tension of water to increase whereas structure breaking salts generally cause the surface tension of water to decrease (Hancer et al., 2001). Salts that are water structure breakers can be floated with either the cationic collector or the anionic collector, whereas salts that are classified as water structure makers stabilize the interfacial water structure at the salt/brine interface and the flotation of these salts with either of these collectors is not possible (Ozdemir et al., 2007). Although calcium is a strong water structure maker cation (Marcus, 1994), it is more effective at the Teflon-water interface than sodium. Here, it appears that the ions have a specific effect due to the fact that calcium is a potential determining ion, and the low salt concentrations (max 0.15 mol/dm^3). Sodium cation is a borderline ion on the structure of water making (Marcus, 1994; Hacer et al, 2001), and is effective at the interface, and brings the zeta potential closer to the positive. As a result, calcium cation more than sodium cation increases the surface tension and surface charge but reduces the contact angle.
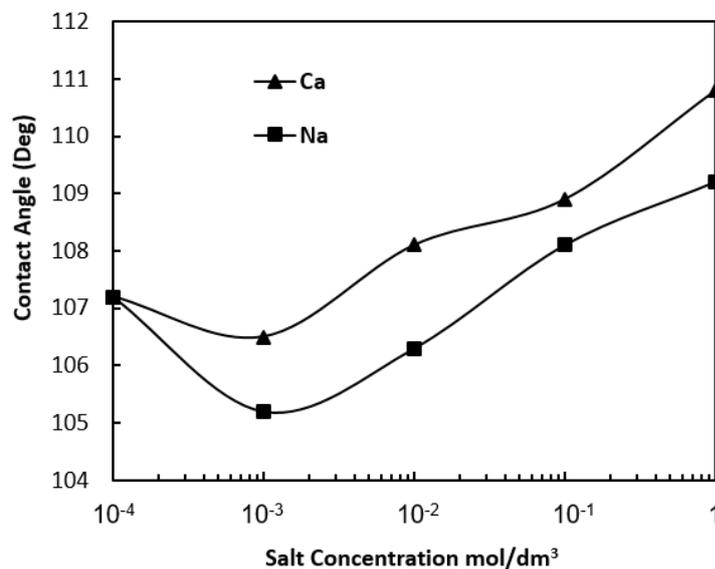
Fig. 7. Contact angles of the plate Teflon as a function of salt concentration

4. Conclusions

The results show that Teflon has a negative surface charge at neutral and all alkali pH's in the presence of NaCl and CaCl$_2$. The zeta potential results showed that as the pH goes from neutral to acidic, the surface charge of Teflon rapidly approaches the positive, and it is positive about pH 3-3.5.

While Ca^{2+} ions more adsorbed on the Teflon surfaces than Na^+ ions, Teflon surface charge was more positive. In addition, it is clear that Ca^{2+} ions are more effective in suppressing the electrical double layer than Na^+.

Especially in the neutral and alkaline pH compared to the IEP region, the zeta potential of Teflon was directly affected by Na^+ and Ca^{2+} ions, but not by Cl^- ions.

The contact angle results also indicated that the natural hydrophobic Teflon has a contact angle of 107º, and when the salt ion concentration increased the contact angle decreased, and calcium chloride is more effective than sodium chloride.

The zeta potential and contact angle results clearly provide a significant insight into the reasons for Teflon natural hydrophobicity. Especially, knowing the surface properties of Teflon in the presence of salt ions may bring the use of Teflon for the mineral processing activities on the agenda.

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