Correction of SAR in salt-affected soils of East Nile Delta (Egypt): Estimation of actual ion concentrations in soil solution

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ABSTRACT

The Sodium Adsorption Ratios (SAR’s) were determined and corrected for ion-pairing and ion-pairing plus activities in saturation extracts of 124 soil samples collected from EL-Hosainiya plain East Nile Delta. The actual ionic concentrations, ionic activities, and ion-pair concentrations were determined using a special computer program. Sulphate ion-pairs occurred in relatively high concentrations with decreasing order of MgSO₄⁺ > CaSO₄⁺ > NaSO₄⁻. Of their total concentrations, the active forms of Ca and Mg were 42% and 50%, respectively. However, it was as much as 70% for Na. A significant change was observed in the SAR values when corrected for ion-pairing and activities. Corrected SAR values for ion-pairing plus activities were as 1.5 times as the uncorrected SAR values. A correction model for SAR values with respect to ion-pair concentrations and activities is performed in this paper.

Key words: Sodium Adsorption Ration; Ion-pairs; Salt-affected Soils; Successive Approximation Technique

Introduction

Plants are detrimentally affected, both physically and chemically, by excess salts in some soils and by high levels of exchangeable sodium in others. Soils with an accumulation of exchangeable sodium are often characterized by poor tilth and low permeability making them unfavourable for plant growth. Sodium adsorption ratio (SAR), along with pH, characterizes salt-affected soils (Munshower, 1994). It is an easily measured property that gives information on the comparative concentrations of Na⁺, Ca²⁺, and Mg²⁺ in soil solutions. The equation used to calculate SAR is given as follows:

\[
SAR = \frac{[Na^+]^3}{0.5 \times (Ca^{2+}) + [Mg^{2+}]} 
\]

[1]

where [Na⁺], [Ca²⁺], and [Mg²⁺] are the concentrations in m.mol/L of sodium, calcium, and magnesium ions in the soil solution.

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The actual concentrations of the ions in soil solution are completely different from the measured concentrations, particularly in high saline soils, with solution of high ionic strength. Nakayama (1969) reported that “We do not obtain a rapid and dramatic improvement in soil physicochemical properties when soils high in free alkali carbonates are treated with Ca salt amendments, namely, that a large part of the Ca that eventually gets into solution is in the inactive form, consequently is unavailable for Na-replacement”. Therefore, the reclamation and management of salt-affected soils required accurate knowledge of the solution chemistry of the major cations and anions existing in the soil solutions and soil extracts. The fraction of cations and anions are so attracted to one another in undiluted solutions that they behave as if unionised; therefore, the analytical concentration used to compute the ionic strength and the ionic activity should take into account the ion-pairs formed (Adams, 1971).

One of the significant features of ion-pair formation in soils is that theoretically the presence of Ca and Mg as ion-pairs should influence ESR (Exchangeable Sodium Ratio)-SAR relationship (Alzubaidi and Webster, 1983). Therefore, some investigators suggested corrections for SAR values for ion-pairing and activity in order that the ESR-SAR relationship becomes more valid for predicting exchangeable sodium percentage (ESP). Babcock and Schulz (1963) studied Na and Ca reactions in chloride and sulphate systems. They concluded that when ESP is calculated from analysis of soil extracts, the analytical data should be expressed in activities rather than concentrations. Roa. T. S. et al. (1968) also studied Na-Ca and Na-Mg ion exchange equilibria for chloride and sulphate systems. They concluded that ion-pair association in addition to activities should be taken into account for ions in the solution phase. However, Bresler et al. (1982) stated that although ESP was originally the main criterion for evaluating sodium contents in soils, emphasis has recently shifted toward the use of SAR of equilibrium soil solution.

The aim of this paper is to correct the SAR’s calculated for different soil samples for ion-pairing and ionic activities. Determine actual ion concentrations and describe kinds and magnitude of major ion-pairs in soil saturation extracts, are included in this paper.

Site and Methods

The investigated area of salt-affected soils in EL-Hosainiya plain, is located in the most north-eastern part of the Nile Delta (31° 57 ': 32° 13 ' E, 30° 51 ': 31° 03 ' N). The Fluvio -marine flats and the river terraces are the main landscapes of the area. The rain-fed is lake cause of the domain climate condition (Mediterranean climate), around (100-200 mm) annual precipitation per year. The Temperature is 31 °C in summer and 12 °C in winter. The soil characterised by a heavy clay texture and high salinity with high exchangeable sodium. The chemical compositions of the saturation extract of 124 soil samples collected from 18 soil profiles were determined for major cations and anions according to Richards (1954).

The determination and calculation of different ion-pairs concentrations, activity coefficients, and the active ion concentrations were processed using a special computer program based on the procedure outlined by Adams (1971).

Theory

Adams (1971) developed a method for correcting for ion-pairing in the calculation of ionic activities and demonstrated a considerable effect of ion-pairing on ionic strength, ionic concentrations, and ionic activities in soil solutions.

The method of correcting for ion-pairing involves: using measured ionic concentrations, \( C^m \), to calculate ionic strength, \( \mu \), assuming no ion-pairing, \(^a\) calculating ionic activities, \( C^0 \), assuming no ion-pairing \(^b\) calculating ion-pair concentrations, \( C^{ip} \), with respective ion-pair equations, equilibrium constants, \( K_i \), and initial estimates of ionic activities, \(^c\) revising ionic concentrations and ionic strength by subtracting the calculated ion-pair concentrations, and \(^d\) repeating steps 2, 3, 4 until all ionic concentrations and activities remain unchanged with succeeding calculations.

In order to calculate the ionic activities, m.mole per litter, the ionic strength, \( \mu \), of the solution fraction then the ionic activity coefficient, \( \gamma \), of each species in the soil solution must be obtained according to the following equations:

\[
\mu = \frac{1}{2} \sum_{i=1}^{n} C_i z_i^2
\]
where \( c_i \) is the concentration of ion species \( i \), \( z_i \) is its valence, and \( n \) is the number of species in the solution. Unlike the formulas used by Adams (1971) and Ostrer and McNeal (1971) in their studies the activity coefficient, \( \gamma_i \), of a solution species, \( i \), was defined in this study by the WATEQ form of Debye-Hückel equation (Truesdell and Jones, 1974) as
\[
\log \gamma_i = \frac{-A z_i^2 \sqrt{\mu}}{1 + B z_i \sqrt{\mu}} + b_i \mu
\]

where \( z_i \) is the ionic charge of aqueous species, \( i \), and \( A \) and \( B \) are constants dependent only on temperature. \( a_i^0 \) and \( b_i \) are ion-specific parameters fitted from mean-salt activity-coefficient data.

Multiplying measured ion concentration, \( C_i^m \), by the activity coefficient, \( \gamma_i \), produces ion activity (active concentration), \( C_i^0 \), of each species, \( i \), in the soil solution as
\[
C_i^0 = C_i^m \times \gamma_i
\]

The ion-pair concentrations, \( C_{ij}^{lp} \), can be calculated using the traditional method for presenting the dissociation of weak electrolytes. Mass action expression of ion-pairs in solution can be represented by
\[
K_i = \frac{(x_i)^{\alpha}(y_i)^{\beta}}{(IP_i)}
\]

where \( (x_i) \), \( (y_i) \), \( (IP_i) \) are cation, anion, and ion-pair activities, respectively. The superscripts, \( \alpha \) and \( \beta \), are stoichiometric coefficients and \( K_i \), is an equilibrium constant. The activity coefficients of ion-pairs are taken as unity. Hence, equation [5] can be reformed as
\[
C_{ij}^{lp} = \frac{(x_i)^{\alpha}(y_i)^{\beta}}{K_i}
\]

where \( C_{ij}^{lp} \) is the \( j \)th ion-pair concentration.

It must be noticed that the ionic concentration of the first approximation is the measured ionic concentration, \( C_i^m \), obtained from chemical analysis. The ionic concentrations in the proceeding approximation, is calculated from the previous ionic concentrations minus the sum of concentrations of that ion present ion-pairs as following:
\[
C_i^r = C_i^{r-1} - \sum_{j=1}^{k} C_{ij}^{lp}
\]

where, \( C_i^r \), is the ionic concentration of the \( r \)th approximation, and \( k \), is the number of ion-pairs per \( i \)th ion species.

The thermodynamical data and constants used for the calculation of ion-pairing and activities were derived from different references (Adams, 1971; Jacobson and Langmuir, 1974; Siebert and Hostetler, 1977; Plummer and Busenberg, 1982).

Computer program

A computer program, for MATLAB 7.1 data processing framework, was developed on the basis of the
calculation mentioned previously, using the successive approximation technique and was applied to this study. A flow diagram of the computation scheme, in which most of the MATLAB coding statements have been reduced to conventional language (algorithm), is presented in Figure 1.

In the initial step the measured molar concentrations, $C^m_i$, fed into the computer with the Statement Data-Entry. Ionic strength, $\mu$, activity coefficients, $\gamma$, and active concentrations $C^0_i$, are calculated with the Statements, $I$, $A_{Coff}$, and $C_{act}$ by equations [2], [3], and [4] respectively. Thermodynamic equilibrium constant, $K_j$, of different ion-pairs in Source Statement $S_{pro}$ are fed into the Statement $C_{ip}$ to produce the molar concentrations, $C_{ij}$, of the different ion-pairs, $j$, of the species, $i$, in the saturations extracts by equation [6].

![Image](image_url)

**Fig. 1:** Scheme of computations in the special computer program for correcting the ionic concentrations for ion-pairing and activities.

Through the Statement $C_A$, the ionic concentrations are corrected for ion-pairing using equations [7], where the ionic concentrations of the previous approximation are reduced by the ion-pairs concentrations. A
Conditional Control Statement, Statement CCS is utilised to test the convergence of the successive ionic concentrations, $C_i$, based on a predetermined threshold.

The computational flow forms a loop (Successive Approximation Loop) from Statements CCS to $I$ and back to CCS until the difference between the successive, $C_i$, equal to the threshold or smaller.

If the convergence condition is fulfilled, the computation flow proceeds out of the loop.

Results and discussion

The soils are mainly saline and/or sodic with sodium chloride being the dominant salt in the soil saturation extracts, and the soluble salt being in the order of NaCl > MgSO$_4$ > CaSO$_4$ > Ca(HCO$_3$)$_2$. The saturation extract analytical data of the 124 samples showed the soil salinity, as expressed in terms of electrical conductivity EC. The EC values varying from 3.19 to as high as 46.3 dS m$^{-1}$ with standard deviation of 9.38, indicating a wide variation ranging from no salinity to extremely high salinity.

The ionic composition of each soil solution was corrected for ion activity and ion-pairing according to the procedure outlined previously using the computer program.

After a specific number of successive approximations for each soil solution sample, the ionic concentrations showed no significant change. Ionic concentrations of the final approximation considered to be the actual concentrations.

The data of the first approximation which actually based on the chemically determined ionic concentrations, and the final approximation calculated by the computer program are presented in Table 1.

<table>
<thead>
<tr>
<th>Ions/Ion-pairs</th>
<th>First Approximation</th>
<th>Final Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration</td>
<td>Activity</td>
</tr>
<tr>
<td></td>
<td>m.mole/litter m.mole/litter</td>
<td>m.mole/litter m.mole/litter</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>27.91</td>
<td>08.55</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>34.44</td>
<td>14.56</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>144.23</td>
<td>104.02</td>
</tr>
<tr>
<td>K$^+$</td>
<td>11.68</td>
<td>07.21</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>85.90</td>
<td>13.50</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>00.00</td>
<td>00.00</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>03.29</td>
<td>02.30</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>128.40</td>
<td>79.64</td>
</tr>
<tr>
<td>Total</td>
<td>435.87</td>
<td>229.81</td>
</tr>
</tbody>
</table>

It was noticed that the ionic strength calculated with respect to ion-pairing is decreased from 0.44 in the first approximation to 0.30 in the final approximation (Table 1).

Ionic concentrations of Ca and Mg are decreased in the final approximation by about 44.1% and 51.13%, respectively, of their concentrations in the first approximation. However, Na ionic concentration decreased only by 3.63% of its concentration in the first approximation.

The concentrations of major kinds of ion-pairs found in the saturation soil extracts are presented in Table 2.

Sulphate ion-pairs MgSO$_4^{o}$, CaSO$_4^{o}$, and NaSO$_4^{i}$ occurred in relatively high concentrations in decreasing order of MgSO$_4^{o}$ > CaSO$_4^{o}$ > NaSO$_4^{i}$, namely 16.74, 11.29, and 5.0 mM/L, respectively. Alzubaidi and Webster (1983) found in their study on ion-pairs in a Solonetzic soil, that the sulphate ion-pairs occurred in relatively high concentrations in decreasing order of NaSO$_4^{i}$ > MgSO$_4^{o}$ > CaSO$_4^{o}$. 

Table 1: Mean average of ionic and ion-pair concentrations and ionic activities of 124 soil saturation extracts, the first and final approximations obtained from the computer program.
Table 2: Ranges and means of major kinds of ion-pairs in 124 soil saturation extracts.

<table>
<thead>
<tr>
<th>Ion-pairs</th>
<th>Concentration (mM/L)</th>
<th>Mean (mM/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaSO₄⁺</td>
<td>0.61 – 36.24</td>
<td>11.29</td>
</tr>
<tr>
<td>CaCO₃⁺</td>
<td>0.00 – 0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CaHCO₃⁺</td>
<td>0.016 – 0.44</td>
<td>0.18</td>
</tr>
<tr>
<td>MgSO₄⁺</td>
<td>0.28 – 55.07</td>
<td>16.74</td>
</tr>
<tr>
<td>MgCO₃⁺</td>
<td>0.00 – 0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>MgHCO₃⁺</td>
<td>0.014 – 0.61</td>
<td>0.21</td>
</tr>
<tr>
<td>NaSO₄⁻</td>
<td>0.125 – 17.30</td>
<td>0.00</td>
</tr>
<tr>
<td>NaCO₃⁻</td>
<td>0.00 – 0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NaHCO₃⁻</td>
<td>0.02 – 0.25</td>
<td>0.10</td>
</tr>
<tr>
<td>KSO₄⁻</td>
<td>0.013 – 0.27</td>
<td>0.07</td>
</tr>
</tbody>
</table>

About 42% of calcium total concentration in the saturation extracts occurred in the form of ion-pairs and it was 50% for magnesium. In other hand sodium had only 4% of its total concentration in ion-pairs forms. Some literatures data was in agreement of the foregoing results. Rance and Davey (1968) found that an equilibrium solution of CaSO₄ contained 32.1% of the total calcium in the form of ion-pairs. Rao et al. (1968) found between 25% and 48% of the soluble Ca or Mg was present as ion pairs, when they studied N-(Ca + Mg) exchange reactions in a sulphate system. In their study Alzubaidi and Webster (1983) reported that for calcium and magnesium, 42.1% and 41.7% of their total concentration present as ion-pairs forms, respectively, in contrast 3.4% only of sodium total concentration is ion-pairs.

The concentrations of Ca, Mg, and Na corrected for ion-pairing once and ion-pairing plus Activities another and the ration (Ca+Mg)/Na are represented in Table 3. It was observed that correcting the concentrations of Ca, Mg, and Na for ion-pairing and for ion-pairing plus activities, decreased the ratio (Ca+Mg)/Na from 0.86 (the initial conc.) to 0.46 (corrected for ion-pairing only); i.e. decreased by approximately 46%, and to 0.26 (corrected for ion-pairing + Activities); i.e. decreased by approximately 70%. Hereby, the expected adsorbed Na on the adsorption complex will increase over (Ca + Mg) more than expected if the initial concentrations used solely.

Table 3: Correction of Ca, Mg, and Na concentrations for ion-pairing and ion-pairing plus activities and its effect on the ratio (Ca +Mg)/Na.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Initial Ion concentration (meq/L)</th>
<th>Ca + Mg</th>
<th>Ion conc. Corrected for ion-pairing (meq/L)</th>
<th>Ca + Mg</th>
<th>Ion conc. Corrected for ion-pairing + Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>55.82</td>
<td>0.865</td>
<td>31.23</td>
<td>0.467</td>
<td>10.47</td>
</tr>
<tr>
<td>Mg</td>
<td>68.89</td>
<td>33.66</td>
<td>15.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>144.23</td>
<td>139.01</td>
<td>100.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The status of Na in one hand and Ca and Mg in another of the salt-affected soils is normally evaluated before performing any reclamation processes. Therefore, it is of interest to compare the active form (available for reaction) of Ca and Mg to the active form of Na in the salt-affected soils particularly sodic soils (Alzubaidi and Webster, 1983).

The Different forms of Mg, Ca, and Na in the soil saturation extracts (Figure 2.) were calculated with respect to ion-pairing and activities. The active forms of total Ca and Mg represent only 20% and 23%, respectively, while approximately 70% of the total concentration of Na in the soil saturation extracts is in the active form.

The sulphate ion-pairs represent 41.32% and 46.38% of the total concentrations of Ca and Mg, i.e. 98.38% and 92.76% of the total Ca and Mg ion-pairs, respectively. While about 03.47% of the total Sodium concentrations in the soil saturation extracts were in the form of sulphate ion-pairs, i.e. about 86.75% of the total Na ion-pairs.

Sodium adsorption ratios (SAR’s) of different soil saturation extracts calculated by equations [1], were corrected with respect to ion-pairing only and ion-pairing plus activities for Ca, Mg, and Na generated by the computer program (Table 4).

Table 4: SAR mean values of 124 soil samples corrected for ion-pairing and ion-pairing plus activity. § SAR, uncorrected: SAR, corrected for ion-pairing only, SAR, corrected for ion-pairing plus activities.

<table>
<thead>
<tr>
<th>SAR,</th>
<th>SAR,</th>
<th>SAR,</th>
<th>SAR, : SAR,</th>
<th>SAR, : SAR,</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.00</td>
<td>22.52</td>
<td>26.83</td>
<td>01.25</td>
<td>01.49</td>
</tr>
</tbody>
</table>
Correcting the concentrations of ions for ion-pairing only and ion-pairing plus activities leads to a significant change in the SAR values. As shown in Table 4, SAR₁, values corrected for ion-pairing only was as 1.25 times as the comparable uncorrected values (SARₒ), however, the similar comparisons for SAR₂, values corrected for ion-pairing plus activities was as 1.49 times as the uncorrected values (SARₒ). These results were in a quite agreement with the results obtained by Alzubaidi and Webster (1983).

The foregoing results emphasise the opinion that the corrections for ion-pairing or even more so for ion-pairing plus activities should be taken into account in order to obtain more accurate SAR values and much closer to the real situation.

The relationship between SAR₂, values corrected for ion-pairing plus activities and uncorrected values (SARₒ) was examined in order to drive a correction model for SAR values. SAR₂ was regressed against SARₒ (Figure 3). The Power relationship gives the most suitable model representing the relationship between SAR₂, values corrected for ion-pairing plus activities and uncorrected values (SARₒ), with R² value “Goodness-of-fit” of 0.968.

When SAR₂, values corrected for ion-pairing plus activities are regressed against the uncorrected values (SARₒ) as shown in Figure 3, the data corresponded reasonably well to a Power regression equation:

\[
SAR_p = 1.167 \times [SAR_o]^{1.081}
\]  \[8\]

where \(SAR_p\), is the predicted sodium adsorption ratio corrected for ion-pairing plus activities.

Equation [8] represents a correction model for SARₒ values calculated based on the chemically determined ionic concentrations.

Conclusions

Measured ionic concentrations do not gives accurate information about dissociation and ion exchange processes in the soil.
Ion-pair formation induced by high salt concentrations strongly influences the effective ionic concentrations that are available for reactions, and consequently the SAR-ESR relationship. In general, sulphate ion-pairs occurred in relatively high concentrations with decreasing order of MgSO$_4$ > CaSO$_4$ > NaSO$_4$ in these soils. With ionic strength ranged between 0.25 and 0.50, taking into account the ion-pair concentrations in the soil saturation extracts, the active forms of Ca and Mg were about 20% and 23%, respectively, of their total concentrations. While the comparable value for Na was as much as 70% of its total concentrations.

Corrected SAR values for ion-pairing plus activities were as 1.50 times as the uncorrected SAR values. Therefore, correcting SAR values for ion-pairing and ionic activities is of the paramount importance before starting the reclamation processes for sodic soils and calculating the gypsum requirements. Equation [8] can be used as a correction model for SAR values calculated using the chemically determined ionic concentrations for EC ranged between 3.19 to 46.3 dS m$^{-1}$ under such soil conditions.

**References**


