



EVALUATION OF SODIUM ION ADSORPTION USING SOME THERMODYNAMIC INDICATORS FOR SOIL SAMPLES AT DIFFERENT LOCATIONS

1- Jinan Hussein Abdul Hasan

jenan.P100819@agre.uoqasim.edu.iq

2- Kadhim Mahdi Jasim

3-Amal Radhi Jubeir

4-Mohammed Sallal Olewi

1,2,3,4 Al-Qasim Green University / College of Agriculture
Department of Soil Sciences and Water Resources

Article history:	Abstract:
<p>Received: 11th October 2022 Accepted: 11th November 2022 Published: 20th December 2022</p>	<p>The study included the selection of soils from three different locations (Al-Qasim district, Al-Kifl district, Al-Mahaweel district) with varying electrical conductivity, and the electrical conductivity values ranged between 2-4 decisions m⁻¹ and others ranging between 8-6 decisions m⁻¹ and more than 12, according to American classification according to plant tolerance. Soil samples were taken from a depth of (0-20) cm (and the results of using thermodynamic criteria for the soil of the study using the Abed (2002) program indicated that the ionic strength ranged between 0.032-0.162 mol.l⁻¹, and the values of ionic activity ranged between 37.922-5.949 mmol L⁻¹, and the results indicated that the arrangement of the ion pair is as follows and for all sites, CaSO₄ and MgSO₄ > Na(SO₄)⁻ > K(SO₄)⁻, and the arrangement of the ions in terms of their participation in the ion pair was It was as follows: sulfate SO₄⁻² > calcium Ca⁺² or magnesium Mg⁺² > bicarbonate HCO₃⁻¹ > sodium Na⁺¹. The free ions were arranged as follows Na⁺¹ > SO₄⁻² > Mg⁺² > Ca⁺² > HCO₃⁻¹ > K⁺. Based on the previous thermodynamic calculations, the concentration of the main ions present was corrected to obtain the actual concentrations and thus reassess the sodium adsorption ratio (SAR). These values were compared with the ratios before the correction, as the SAR values ranged between 2.321-8.765 before the coupling, while after the ion coupling (ions Al-Hurra) ranged between 2.693 - 9.396.</p>

Keywords: thermodynamic indicators, ion coupling, sodium ion adsorption, ionic strength, ionic activity.

INTRODUCTION

Using thermodynamic standards to accurately express the chemistry of ions. And that chemical equilibrium reactions are controlled by the equilibrium constant, as the thermodynamic chemical equilibrium is evidence of predicting the behavior of the system and knowing which metal controls the solubility (Dreher, 1997). There are several methods for calculating thermodynamic parameters, including the Adam Soil solution program, (1971) and the program that he used. (2002, Abed) for calculating some thermodynamic parameters and free ions, as well as estimating ionic pairs present in soils. Note Bandyopadhyay, Goswami (1985), and Walt (1999) the success of using these criteria in revealing the relationship between the amount of the ion on the exchange complex and its concentration in the equilibrium solution, including the ionic activity, which is a thermodynamic criterion that reflects the effect of the concentration and type of soil solution components on the activity of the ion when evaluating the state of the ion, especially The soluble formula in the soil solution, and the ionic activity is a basic thermodynamic value used in calculating all thermodynamic parameters. (Al-Rubaie, 2002) stated that the use of thermodynamic criteria, including the ionic activity of potassium, the coefficient of activity, the relationship of capacity and intensity (I/Q), free energy, and the regulatory capacity of potassium was successful in assessing the strength of potassium readiness in different Iraqi soils.

Hoffman (2010) indicated that the SAR values are a function of soil salinity, as the higher the soil salinity, the greater the harmful effect of sodium. In light of this, several attempts emerged to describe the ion exchange in soils affected by salinity, including the equations of action of mass, energy, and thermodynamics. Abd (2012) reported that the

coefficient of activity for divalent ions is less than it is for monovalent ions when drawing the relationship between the ionic strength and the coefficient of ionic activity. He also noted that a correction for ionic coupling and high led to a decrease in the correlation coefficient between the ionic strength and the concentration of these ions compared to what is it before the correction, and this indicates the participation of ions in ionic activity and ion coupling. Al-Sultani (2015) mentioned that there is an inverse relationship between the values of the ionic activity coefficient and the ionic strength, as the values of the ionic effectiveness coefficient ranged between 0.589_0.288, so the lowest value was recorded for the soil of Abu Gharq irrigated with tap water with high ionic strength, and the highest value for the soil of Alexandria. irrigated with river water of low ionic strength.

MATERIALS AND METHODS

1-Collecting samples and preparing them for the study:

The study included the selection of soil from three different locations (Al-Qasim district, Al-Kifl district, and Al-Mahaweel district), varying in electrical conductivity according to the American classification and according to plant tolerance, as it ranged between 4-2 siemens m-1 and others ranging between 8-6 siemens m- 1 and more than 12, and soil samples were taken from a depth of (0-20) cm. Soil samples were placed in plastic bags and transported for air drying, then ground with a wooden hammer and passed through a sieve with a diameter of 2 mm. The electrical conductivity was measured in the saturated soil paste extract using a device. EC - Meter type WTW and according to the method described by Richards ((1954). Positive and negative ions were also estimated in the soil paste extract according to the method described in ICARDA (John Ryan, 2003).

2-The use of some thermodynamic parameters in the study of soil samples

Some thermodynamic parameters were estimated using Abed (2002) software to calculate: -

A- Ionic strength

The first method is calculated according to the Lewis and Randall equation, which depends on the concentration and nature of the ions and the charge of the ion, which states: -

$$I = 1/2 \sum C_i \cdot Z_i^2$$

The second method is according to the equation (Griffin and Jurinak, 1973) mentioned in Sposito(2008).

$$I = 0.013 * EC$$

And EC means the electrical conductivity of the Dissie-Siemens M-1 equilibrium solution.

I stand for ionic strength and is measured in mill

B-Activity coefficient:

Calculated from the Debye equation and the structure (Debye and Huckel) :

$$\text{Log } f_i = -A Z_i^2 \cdot (I)^{0.5} / 1 + B d_i \cdot (I)^{0.5}$$

Where:

f_i – is the activity coefficient of the ion (i).

Z_i - valency of the (i) ion.

A- a constant of 0.509 at a temperature of 25 °C.

B - a constant of $10 * 0.3288$ for water at a temperature of 25 °C

d_i – represents the diameter of the ion

I- means ionic strength and is measured in mol liter

Ion activity

$$C- a_i = f_i * C_i$$

where:

a_i stands for – the ionic activity of ion (i) mmol l-1.

f_i – the activity coefficient of the ion (i).

C_i – the concentration of the ion (i) in millimoles L-1

D- Ion Pairs

RESULTS AND DISCUSSION

The use of some thermodynamic parameters for the study soils Abed's` 1 (2002) program was used to calculate some of the following thermodynamic parameters.

1-Ionic pairing

Table 1 indicates the dominance of the double sulfate ions over the rest of the ions and in all the studied sites, and these ions increase with the increase of salts and the concentration of ions. Mono-positive (Adams, 1971). The results indicated that the arrangement of the ion pair is as follows and for all sites $CaSO_4$ and $MgSO_4 > Na(SO_4) > K(SO_4)$ -. As for the arrangement of the ions in terms of their participation in the ion pair, it was as follows: Sulfate $SO_4^{2-} >$ Calcium Ca^{2+} or magnesium $Mg^{2+} >$ bicarbonate $HCO_3^- >$ sodium Na^+ , that the contribution of sulfate in a greater percentage in ion pairing is attributed to the high affinity of co-ion pairing with divalent ions. The overlapping of ions and their behavior and the formation of ion doubles in large numbers and concentrations in the soil solution lead to the fact that routine analytical methods do not differentiate between the real ion concentration and the concentration of its double ions, and the real concentration of the ion is usually less than the laboratory

measured concentration. We also note from the table that the concentration of the double ion Na(SO₄)⁻ ranges between 0.054 - 0.394 mmol L⁻¹ and the highest concentration was in the Al-Kafil site S3 and the lowest concentration was in the converters site S1.

Table 1: Ion Pairs for study soil samples (mmol L⁻¹)

Depth (0 - 20) cm/mmol L ⁻¹						sample icon	Location
Mg(HCO ₃) ⁺	Ca(HCO ₃) ⁺	K(SO ₄) ⁻	Na(SO ₄) ⁻	MgSO ₄ ⁰	CaSO ₄ ⁰		
0.123	0.119	0.017	0.140	1.704	1.470	S1	Qasim
0.209	0.181	0.017	0.174	2.515	1.947	S2	
0.264	0.240	0.017	0.168	2.583	2.091	S3	
0.228	0.310	0.012	0.259	1.715	2.079	S1	Al-Kafil
0.272	0.368	0.016	0.306	2.047	2.475	S2	
0.427	0.401	0.016	0.394	2.851	2.391	S3	
0.057	0.050	0.011	0.054	0.828	0.646	S1	Al-Mahaweel
0.103	0.075	0.006	0.065	1.203	0.784	S2	
0.185	0.140	0.011	0.183	1.640	1.107	S3	

2-Free Ions

The results of Table 2 indicate that the free sodium ions ranged between 50.565 - 6.496 mmol L⁻¹, and the lowest value was in the denominator site S1 and the highest was in the denominator site S3, and that the lowest value was in the denominator site S1 and the highest was in the site of the denominator S3, which represents soils with a high content of Sodium, where the arrangement of the free ions was as follows: Na¹⁺ > SO₄²⁻ > Mg²⁺ > Ca²⁺ > HCO₃¹⁻ > K⁺. As for the free chloride ions in the study soils, they ranged between 55,000-8,990 mmol L⁻¹, and the lowest value was in the denominator site S1 and the highest value was in Sponsorship site S3.

Table2 The main free ions in the study soil samples (mmol L⁻¹)

Free ion concentration in mmol L ⁻¹ / depth (0 - 20) cm						sample icon	Location
SO ₄ ²⁻	HCO ₃ ¹⁻	K ¹⁺	Na ¹⁺	Mg ²⁺	Ca ²⁺		
7.969	3.399	0.583	10.970	5.573	4.610	S1	Qasim
8.326	3.910	0.773	16.946	10.086	8.189	S2	
8.281	4.706	0.803	16.912	10.852	9.261	S3	
7.466	5.461	0.638	29.531	8.187	9.773	S1	Al-Kafil
8.507	6.000	0.804	32.334	9.211	11.049	S2	
7.888	5.843	0.964	50.565	16.043	13.555	S3	
4.612	2.244	0.609	6.496	3.626	2.650	S1	Al-Mahaweel
5.062	2.951	0.344	7.645	5.314	3.271	S2	
6.409	4.325	0.569	21.067	7.595	4.960	S3	

3-Ionic strength

The ionic strength is the most expressive of the role of the solution in the reactions, and it directly affects the effectiveness or the effectiveness coefficient. Table 3 shows that its values ranged between 0.032 - 0.162 mol.L-1.

4-Ionic activity

The ionic activity is of great importance in calculating the thermodynamic criteria, as the criterion is used here to evaluate the state of some ions, including sodium, and Table 3 shows that the ionic activity values range between 37.922-5.949 mmol L-1, which is a salt-affected soil and is characterized by its high levels of Sodium and chloride

Table 3 ionic strength (mol L-1) and ionic activity (mmol L-1) for the study soil samples

Ionic activity mmol L-1 / depth (0 - 20) cm						ionic strength mol l-1	sample icon	Location
SO ₄ ²⁻	HCO ₃ ¹⁻	K ¹⁺	Na ¹⁺	Mg ²⁺	Ca ²⁺			
3.685	3.115	0.496	9.103	2.719	2.095	0.052	S1	Qasim
3.149	3.067	0.596	13.289	4.697	3.246	0.084	S2	
3.053	3.667	0.614	13.179	4.975	3.596	0.091	S3	
2.711	4.240	0.486	22.925	3.719	4.025	0.097	S1	Al-Kafl
2.954	4.606	0.604	24.823	4.073	4.398	0.110	S2	
2.495	4.382	0.705	37.922	6.717	5.03	0.162	S3	
2.360	1.898	0.511	5.494	2.062	1.436	0.032	S1	Al-Mahaweel
2.440	2.459	0.284	6.370	2.899	1.687	0.039	S2	
2.605	3.453	0.448	16.821	3.699	2.230	0.071	S3	

5- Sodium adsorption ratio (SAR) before correction for ion coupling and after correction

This ratio expresses the intensity of the sodium ion in the liquid soil phase according to the Ratio Law of SP. , 1940 to the square root of calcium and magnesium, as the results are shown in Table 4 indicate that the variation of the chemical and physical properties of the soils have a significant impact on the variation in the values of the sodium adsorption ratios. S1 terminal site. The high values of SAR values in soils affected by salts collect the effect of irrigation operations, both quantitatively and qualitatively, on the sodium percentage values in the brine soil solution. These results agreed with what was reached by (Abdullah, 2006), who found that the sodium adsorption rate (SAR) increased with the increase in soil salinity, which negatively affected soil properties and composition, and thus the growth of apps. Based on the thermodynamic calculations, the concentration was corrected for the main ions present in obtaining the actual concentrations, and therefore the sodium adsorption ratio SAR was re-evaluated. These values were compared with the ratios before correction. Table 4 shows these calculations. The SAR value after ion pairing ranged between 2.693 – 9.396.

It can be concluded that the correction of ion pairing increased the SAR values of sodium adsorption and thus changing the critical limits within this indicator, which may shift the classification of soil according to the sodium adsorption rate from one class to another, and this is of great importance in soil reclamation, especially with a high concentration of sodium, and this is consistent with With what I have reached (Al-Asadi, 2018).

Table 4: Sodium adsorption ratio before correction for ion coupling and after correction in mmol L-1

Depth (0 - 20) cm		sample icon	Location
SAR after correction	SAR before correction		
3.435	3.010	S1	Qasim
3.964	3.560	S2	
3.778	3.401	S3	

6.979	6.318	S1	Al-Kafil
7.177	6.482	S2	
9.396	8.765	S3	
2.693	2.321	S1	Al-Mahaweel
2.610	2.352	S2	
5.659	5.368	S3	

CONCLUSIONS:

1-The arrangement of the ion pair for all sites was as follows: CaSO_4 and $\text{MgSO}_4 > \text{Na}(\text{SO}_4)^- > \text{K}(\text{SO}_4)^-$, and the order of the ions in terms of their participation in the ion pair was as follows: sulfate $\text{SO}_4^{2-} >$ calcium Ca^{+2} or magnesium $\text{Mg}^{2+} >$ Bicarbonate $\text{HCO}_3^- >$ Sodium Na^{+1} .

2-The values of the ionic activity of sodium ions in soils of varying salinity ranged between 37.922-5.494 mmol L⁻¹ for a depth of (0-) 20 cm...

RECOMMENDATIONS

1-The needs to use thermodynamic criteria such as ionic activity and ion coupling in correcting the values of SAR and Adj RNA in some soils because of their effect on the relationship between SAR and ESR.

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