



A study of some thermodynamic parameters in Babylon province

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Abstract

The study included the selection of soil from three different locations (Al-Moradia area, Al-Moradia research station, Al-Kifl district, Abi Gharqa subdivision, Abu Gharqa Agriculture Division) varying in electrical conductivity, and electrical conductivity values ranged between 4-2 Ds.m⁻¹ and another ranging between 8-6 Ds.m⁻¹ and more than 12 according to the American classification and according to the plant's tolerance. Soil samples were taken from two depths (0-20), (20-40 cm). The results of using thermodynamic standards for the study soil using the Abed program (2002) indicate that the ionic strength in it ranged between 0.032 - 0.162 mol. L⁻¹ in depth -0 (20 cm). As for the depth (-20) 40 cm, its values ranged between 0.036 - 0.167 mol. L⁻¹, and the ionic activity values for depth (-20 cm) ranged between 37.922-5.949 mol. L⁻¹ and 38,078 - 5.521 mol. L⁻¹ for depth -20 (40 cm, The results indicated that the arrangement of the ionic double is in the following form and for all sites CaSO₄ and MgSO₄ > Na(SO₄)⁻ > K(SO₄)⁻, The arrangement of the ions in terms of their participation in the ion pairing was as follows: sulfate SO₄⁻² > calcium Ca⁺² or magnesium Mg⁺² > bicarbonate HCO₃⁻¹ > sodium Na⁺¹. As for the free ions, their arrangement was 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 in order to obtain the actual concentrations, and thus the sodium adsorption ratio was re-evaluated. These values were compared with the ratios before the correction. The SAR values before pairing ranged from 2.217-8.367 for depth (0-20 cm, As for the depth (40-20) cm, the values of SAR ranged between 2.206-8.404, while after ionic coupling (free ions) it ranged between 2.593-9.296 for depth (0-20 cm, while for depth (40-20) cm, the values of SAR between 2.438 - 9.131.

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Key Words: thermodynamic parameters, Adam Soil solution program, free ions

DOI Number: 10.14704/NQ.2022.20.11.NQ66288

NeuroQuantology 2022; 20(11):2810-2817

Introduction

The use of thermodynamic parameters to accurately express the chemistry of ions and the chemical equilibrium reactions are controlled by the equilibrium constant, where the thermodynamic chemical equilibrium is an index to predicting the behaviour of the system and knowing which metal controls the dissolution according to (Dreher, 1997). There are several methods for calculating the thermodynamic parameters, including the Adam Soil solution program, (1971) and the program that was used (2002, Abed) to calculate some thermodynamic parameters and free ions, as well as the estimation of the ionic pairs present in soils. Bandyopadhyay, Goswami (1985), Walt (1999) noted the success of using these criteria in revealing the relationship between the amount of ion on the

equilibrium solution, including the ionic activity, which is a thermodynamic criterion that reflects the effect of the concentration and type of components of the soil solution on the effectiveness of the ion when evaluating the state of the ion, especially The formula for solubility in a 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 parameters, including the ionic activity of potassium, the activity coefficient, the amplitude and intensity relationship (I/Q), the free energy and the organizational capacity of potassium, was successful in assessing the strength of potassium availability in different Iraqi soils. Hoffman, (2010) indicated that the SAR values are a function of soil salinity, as the higher the salinity of the soil, the

exchange complex and its concentration in the



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greater the harmful effect of sodium. In light of this, several attempts emerged to describe ion exchange in salinity-affected soils, including mass-energy and thermodynamic equations. Abd (2012) reported that the coefficient of activity for divalent ions is less than it is for monovalent ions when drawing the relationship between ionic strength and ionic reactivity coefficient. On it before correction, this indicates the participation of ions in ionic activity and ionic duplication. Al-Sultani (2015) stated that there is an inverse relationship between the values of the ionic activity coefficient and the ionic strength, as the values of the ionic activity coefficient ranged between 0.589_0.288. The lowest value was recorded when Abu Gharq soil was irrigated with high ionic strength sedimentation water, and the highest value was recorded in Alexandria soil irrigated with river water of low ionic strength.

Materials and methods

1-Collect samples and prepare them for study

The study included the selection of soil from three different locations (Al-Muradia area, Al-Muradia research station, Al-Kifl district, Abi Gharqa district, Abu Gharqa Agriculture Division), varying in electrical conductivity according to the American classification and according to the plant tolerance, as it ranged between 4-2 ds.m⁻¹ and another Ranging from 8-6 ds.m⁻¹ and more than 12, Soil samples were taken from two depths (0-20), (20-40 cm), the soil samples were placed in plastic bags and transported for the purpose of air drying, then ground with a wooden mallet and passed through a sieve with holes 2 mm in diameter, and the electrical conductivity was measured in the saturated soil paste extract Using the EC-Meter type WTW and according to the method described by Richards (1954). The positive and negative ions in the soil pulp extract were also estimated according to the method described in ICARDA (John Ryan, 2003).

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

Some thermodynamic parameters were estimated using the Abed (2002) program to calculate:

1-Strength Ionic

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: -

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

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

$$I = 0.013 \cdot EC$$

and EC stands for the electrical conductivity of Ds. m⁻¹ equilibrium solution.

I stands for ionic strength and is measured in moles. L⁻¹.

2 - Activity coefficient

It is calculated from the Debye equation and the Debye and Huckel structure:

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

So, f_i - the activity coefficient of the ion (i).

Z_i - valence of the ion (i).

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

B - a constant of $10 \cdot 0.328 \cdot 8$ for water at a temperature of 25 °C.

d_i - represents the diameter of the ion

I- stands for ionic strength and is measured in mol L⁻¹.

3- The activity ion

$$a_i = f_i \cdot C_i$$

a_i means - the ionic activity of the ion (i) mol L⁻¹.

f_i - activity coefficient of the ion (i).

C_i - concentration of the ion (i) in mol L⁻¹.

4 ionic couplings. Ion Pairs

Results and discussion

The use of some thermodynamic criteria for the study of soil

The program Abed (2002) was used to calculate some of the following thermodynamic parameters:

1- ionic coupling

Table 1 indicates the dominance of the binary paired sulfur ions over the rest of the ions and in all the studied locations, and these ions increase with the increase in salts and concentration of ions, and this corresponds to the basic principles of ionic pairing, which indicates an increase in the ion pairing of sulfate ions SO₄⁼ with binary positive ions, and decreases with ions positive mono(Adams, (1971) The results indicated that the arrangement of the ion pair is as follows for all sites CaSO₄ and MgSO₄ > Na(SO₄)- > K(SO₄)-, and the arrangement of the ions in terms of their participation in the ion pairing was as follows: sulfate SO₄²⁻ > Calcium Ca²⁺ or magnesium Mg²⁺ > bicarbonate HCO₃⁻ 1> sodium Na¹⁺, The



contribution of sulfate in a greater percentage in the ionic coupling is due to the high affinity for the participation in the ionic coupling with the positive binary ions. The interference of ions and their behaviour and the formation of the ionic pair in large numbers and concentrations in the soil solution leads that the 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 concentration measured in the laboratory. We also note from the table that the

concentration of the double ion $\text{Na}(\text{SO}_4)^-$ ranges between 0.054 - 0.394 mmol .L-1 with respect to the

depth (- 0 (20 cm) and the highest concentration was in the Al-Kifl site S3 and the lowest concentration in the Abi Gharq site S1. As for the depth (40-20 cm, the double ion concentration was $\text{Na}(\text{SO}_4)^-$ ranged between 0.057-0.405 mmol .L-1, and the highest concentration was in Al-Kifl site S3 and the lowest concentration in Abi Gharq site S1.

Table 1. Ion Pairs for Study Soil Samples (mmol L-1)



Depth (0 - 20) cm / mmol l-1						sample code	Location
Mg(HCO3) ⁺	Ca(HCO3) ⁺	K(SO4) ⁻	Na(SO4) ⁻	MgSO40	CaSO40		
0.123	0.119	0.017	0.140	1.704	1.470	S1	Al-Muradia
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-kufl
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	Abi Gharqa
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	
Depth (20 - 40) cm / mmol l-1						sample code	Location
Mg(HCO3) ⁺	Ca(HCO3) ⁺	K(SO4) ⁻	Na(SO4) ⁻	MgSO40	CaSO40		
0.145	0.135	0.020	0.150	1.979	1.644	S1	Al-Muradia
0.223	0.212	0.017	0.175	2.475	2.103	S2	
0.283	0.262	0.018	0.193	2.622	2.165	S3	
0.241	0.342	0.017	0.308	1.933	2.454	S1	Al-kufl
0.302	0.391	0.018	0.316	2.136	2.465	S2	
0.532	0.500	0.017	0.405	3.056	2.562	S3	
0.090	0.085	0.006	0.057	0.958	0.812	S1	Abi Gharqa
0.131	0.108	0.007	0.081	1.222	0.902	S2	
0.185	0.176	0.012	0.190	1.678	1.428	S3	

2- free ions

The results of Table 2 indicate that the free sodium ions in the depth (0 - 20 cm) ranged between 50.565 - 6.496 mmol .L-1, and that the lowest value was in Abi Gharq site S1 and the highest in Al-Kifl site S3.As for the depth (-20) 40 cm, the free sodium ions ranged between 6.583 -50.83 mmol .L-1, and the lowest value was in the Abi Gharq site S1

and the highest in the Al-Kifl site S3 which represents soils with a high content of sodium.Where the order of the free ions was in the following form: Na 1+ > SO4 2-> Mg 2+ > Ca 2+ > HCO3 1- > K+. As for the free chloride ions in the study soils for depth (20) cm, they ranged between 55.000-8.990 mmol L-1 and the lowest value in Abi drowning site S1 and the highest value in Al-Kifl



site S3. As for the depth (-20) 40 cm, the free ions of the highest value was in Al-Kifl site S2. chloride ranged between 53.950 -10.230 mmol L-1 and the lowest value was in Abi Drak site S1 and

Table 2. The main free ions in the study soil samples (mmol L-1)

Free ion concentration mmol l-1 / depth (0 - 20) cm						sample code	Location
SO42-	HCO31-	K1+	Na1+	Mg2+	Ca2+		
7.969	3.399	0.583	10.970	5.573	4.610	S1	Al-Muradia
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-kufi
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	Abi Gharqa
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	
Free ion concentration mmol l-1 / depth (20-40) cm						sample code	Location
SO42-	HCO31-	K1+	Na1+	Mg2+	Ca2+		
8.646	3.631	0.690	11.270	6.286	5.036	S1	Al-Muradia
8.249	4.165	0.793	17.435	10.232	9.142	S2	
8.322	4.895	0.892	19.937	11.405	9.973	S3	
8.568	5.747	0.793	31.612	8.386	10.528	S1	Al-kufi
8.494	6.307	0.912	34.134	9.871	11.329	S2	
8.111	6.968	0.973	50.835	16.852	14.243	S3	
5.027	3.255	0.314	6.583	4.073	3.251	S1	Abi Gharqa
5.319	3.761	0.403	9.529	5.477	3.838	S2	
6.902	4.569	0.638	22.020	7.979	6.603	S3	

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 in depth (-0 (20 cm). As for the depth - 20 (40 cm), its values ranged between 0.036 - 0.167 mol L⁻¹ as the lowest value is found in the site of Abi Gharq S1 and the highest value is found in Al-Kifil site S3.

standard is used here in evaluating the state of some ions, including sodium, and Table 3 shows that the ionic activity values for depth (-0 (20 cm) range from 37.922-5.949 mmol L⁻¹,The depth is - 20 (40 cm). The value of the ionic activity ranges between 38.078 - 5.521 mmol L⁻¹, as the lowest value is found in Abi Gharq site S1 and the highest value is in Al-Kifl site S3 which is a soil affected by salts as well as it is characterized by containing high levels of sodium and chloride .

4- Ionic activity

The ionic activity is of great importance in calculating the thermodynamic parameters, as the

Table 3. Ionic strength (mol L⁻¹) and ionic activity (mmol L⁻¹) for study soil samples

Ionic activity mmol l-1 / depth (0 - 20) cm						ionic strength mol liter-1	sample code	Location
SO42-	HCO31-	K1+	Na1+	Mg2+	Ca2+			
3.685	3.115	0.496	9.103	2.719	2.095	0.052	S1	Al-Muradia
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-kufil
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	Abi Gharqa
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	
Ionic activity mmol l-1 / depth (20-40) cm						ionic strength mol liter-1	sample code	Location
SO42-	HCO31-	K1+	Na1+	Mg2+	Ca2+			
3.868	3.319	0.583	9.310	3.009	2.231	0.057	S1	Al-Muradia
3.080	3.255	0.609	13.628	4.726	3.585	0.088	S2	
2.994	3.791	0.677	15.441	5.151	3.796	0.099	S3	
3.032	4.432	0.600	24.381	3.750	4.250	0.105	S1	Al-kufil
2.905	4.823	0.682	26.102	4.325	4.456	0.116	S2	
2.553	5.219	0.711	38.078	7.037	5.267	0.167	S3	



2.488	2.730	0.261	5.521	2.263	1.714	0.036	S1	Abi Gharqa
2.468	3.104	0.329	7.864	2.911	1.918	0.045	S2	
2.646	3.617	0.496	17.416	3.762	2.858	0.079	S3	

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

This ratio expresses the strength of the sodium ion in the liquid phase of the soil according to the Ratio Law of SP. , 1940 to the square root of calcium and magnesium, The results shown in Table 4 indicate that the variation in the chemical and physical properties of soils has a significant impact on the variation in the values of sodium adsorption ratios. The highest SAR value was recorded before ionic coupling with respect to depth (0-20 cm) at Al-Kifl site S3 8.367, and the lowest value recorded was 2.217 in Abu Gharq site S1. As for the depth (20-40) cm, the highest SAR value was recorded in Al-Kifl site S3, which is 8.404, and the lowest value was 2.206 in Abu Gharq site S1. The high values of SAR values in soils affected by salts clearly reflect the effect of quantitatively and qualitatively irrigation operations on the values of sodium in the soil brine solution. These results are in agreement with the findings of (Abdullah, 2006), which found that the rate of sodium adsorption (SAR) increases with the

increase of soil salinity, which negatively affected the properties and composition of the soil and consequently the growth of agricultural crops. Based on the thermodynamic calculations, the concentration of the main ions present was corrected in order to obtain the actual concentrations and thus he re-evaluated the sodium adsorption rate SAR and these values were compared with the ratios before correction and a table showing these calculations. 2.593 - 9.296, as for the depth (20-40) cm, the SAR values ranged between 2.438 - 9.131, and the highest value was in the Al-Kifl site S3 and the lowest value in the Abu Gharq site S1 for both depths. It can be concluded that the correction of ionic duplication increased the values of sodium adsorption SAR and thus changed the critical limits within this indicator, which may transform the classification of soil according to the rate of sodium adsorption from one class to another, This is of very great importance in soil reclamation, especially with a high concentration of sodium, and this is consistent with what I have reached (Al-Asadi, 2018).

Table 4 Sodium adsorption ratio before correction for ionic coupling and after correction mmol L⁻¹

Depth (0 - 20) cm		sample code	Location
SAR after correction	SAR before correction		
3.435	3.010	S1	Al-Muradia
3.964	3.560	S2	
3.778	3.401	S3	
6.979	6.318	S1	Al-kufl
7.177	6.482	S2	
9.296	8.534	S3	
2.593	2.336	S1	Abi Gharqa
2.610	2.352	S2	
5.659	5.368	S3	
Depth (20-40) cm		sample code	Location
SAR after correction	SAR before correction		
3.347	2.925	S1	Al-Muradia
3.965	3.305	S2	
4.319	3.90	S3	
7.275	6.534	S1	Al-kufl
7.426	6.702	S2	
9.131	8.352	S3	



2.438	2.184	S1	Abi Gharqa
3.128	2.815	S2	
5.762	5.225	S3	

Conclusions

1. The arrangement of the ionic pairs for all sites was as follows: CaSO₄ and MgSO₄ > Na(SO₄)- > K(SO₄)-, and the order of the ions in terms of their participation in the ion pairing was as follows: sulfate SO₄²⁻ > Calcium Ca⁺² or Magnesium Mg²⁺ > Bicarbonate HCO₃⁻ > Sodium Na¹⁺.
2. The values of ionic activity of sodium ion in soils of varying salinity ranged between 5.494-37.922 mmol L⁻¹ for depth (0 - (20) cm and 5.521-38.078 mmol l⁻¹ for depth (20-40) cm.

Recommendations

1. The necessity of using thermodynamic criteria such as ionic activity and ionic duplication in correcting the values of SAR and Adj RNA in some soils due to their effect on the relationship between SAR and ESR.

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