

ASSESSING THE EFFECT OF INDIVIDUAL ELECTROLYTES AND THEIR DISSOLVED IONIC CONCENTRATIONS ON THE EVAPORATION OF DEAD SEA WATER BY DATA OBTAINED FROM LABORATORY EXPERIMENT

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ABSTRACT

It is important to study the evaporation of different electrolyte solutions to simulate evaporation of hyper saline water bodies like the Dead Sea since evaporation behaviour deviates from fresh water when salts are dissolved in fresh water. The dissolved salts lower the vapour pressure of salt water, causing a decrease in evaporation rate. Hence, standard evaporation calculation methods cannot be applied for the evaporation of saline water bodies. Composition of dissolved compounds and their ionic concentrations should be accounted to evaporation calculating models in salt water bodies. Depending on type of electrolyte (1:1, 1:2 and 1:3), evaporation pattern changed and similar numbered electrolytes (CaCl₂ and MgCl₂) exhibited parallel evaporation patterns. The evaporation rate of an electrolyte depends on the number of ions particles into which the solute dissociates and the concentration of each dissociated ion. The evaporation rate of solution decreased with increasing ion concentration until saturation. After saturation concentration, the evaporation rate dropped to its minimum and evaporation continues at its non-zero minimum constant rate of evaporation.

Key words : Dead Sea, Evaporations, electrolytes

1.0 INTRODUCTION

Dead Sea is located in a special geographical place in the world. It is located in the lowest elevation of earth and in an extremely dry land. Due to this land formation, Dead Sea has become one of the most salty water bodies on earth. Dead Sea continuously gets enriched with salty water which comes from surrounding mountains through rivers. However, there are no rivers taking water out of the Dead Sea. The only way to remove water from the Dead Sea is by evaporation. The process of evaporation removes only water and it leaves all dissolved minerals in the Dead Sea, making the sea saltier. Due to this reason Dead Sea consists of two stratified layers. The topmost layer has high density and high salinity compared to the lower layer.

General evaporation models are no longer valid for saline water bodies (Asmar and Ergenzinger, 1999). Therefore, it is important to study Dead Sea evaporation in relation to dissolved salts (Oroud, 1995) Therefore, the effect of individual ions and interactions of ions should be accounted when the evaporation model is developed. Brine evaporation rate can be modeled as a function of dissolved salts using mathematical and empirical relationships (Martin, 1983).

The main objective of this study is to assess evaporation behavior of different electrolyte solutions separately and to compare them with the evaporation behavior of artificial Dead Sea solution. The study will provide information about the pattern of electrolyte solution evaporation to construct evaporation models for saline water bodies.

2.0 METHODOLOGY

Four electrolyte solutions (NaCl, MgCl₂, CaCl₂, Al(NO₃)₃) and 50% diluted Dead Sea sample were tested under laboratory environment. Those samples were dried in an oven at 40 °C for 10 days. Evaporation was measured by weight lost at 40 °C. Density and salinity measurements were taken daily. To obtain the density, 25µml is pipetted out from brine solution into plastic bottle and it is weighted using analytical balance. Density is calculated using equation 01. Concentration of each solution is calculated based on density using equation 02, where all the densities are in g/liter while Molar mass is in g/mol. The density of water is considered at 40 °C.

$$\text{Density of solution} = \frac{\text{Weight}_{\text{solution+empty_bottle}} - \text{Weight}_{\text{empty_bottle}}}{\text{Pipetted_volume}}$$

..... (Equation 01)

$$\text{Concentration of solution} = \frac{\text{Density}_{\text{solution}} - \text{Density}_{\text{water}}}{\text{Molar_Mass_of_electrolyte}}$$

..... (Equation 02)

3.0 PRINCIPLES

The principle of evaporation process is described using the notion of vapour pressure. Evaporation is the process of equilibrating the vapour pressure of liquid to the equilibrium partial vapour pressure of the liquid in the air. The rate of evaporation can reduce due to lowering vapour pressure of liquid and/or increasing the partial vapour pressure of the liquid in the air. In the Dead Sea, both these phenomena occur. Dissolved salts in Dead Sea water decrease the vapour pressure of

liquid while development of high humid layer over the water surface increases the partial vapour pressure of liquid in air phase (Asmar and Ergenzinger, 1999). This experiment focused on effect of dissolved salts on evaporation that is based on changes in vapour pressure in liquid due to dissolved salts or salinity.

The pure liquid solvent has entropy that reflects the moment of its molecules. The entropy of liquid increases due to presence of solute (salt) in liquid. Because of higher entropy of salt solution than that of pure water, there is a weaker tendency to evaporate in salt solution. Therefore, dissolving of salts results in a lowered vapour pressure (Atkins P.W., 1998).

Dissolved solute changes the mole fraction of solvents. According to Raoult's law, vapour pressure of solvent reduces (Equation 03).

$$P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}} \quad \dots\dots\dots(\text{Equation 03})$$

Therefore always, $P_{\text{solvent}} < P^{\circ}_{\text{solvent}}$, hence $\chi_{\text{solvent}} < 1$

Where,

P_{solvent} = vapour pressure of the solvent in solution,

χ_{solvent} = mole fraction of the solvent

and $P^{\circ}_{\text{solvent}}$ = vapour pressure of the pure solvent.

However, the total pressure of a solution equals to the sum of the partial pressures of the solvent and solute (Equation 04). If the salt is considered as non volatile, solute vapour pressure becomes zero and vapour pressure of solution can be explained as in Equation 05.

$$P_{\text{solution}} = P_{\text{solvent}} + P_{\text{solute}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}} + \chi_{\text{solute}} P^{\circ}_{\text{solute}} \quad \dots\dots\dots(\text{Equation 04})$$

$$P_{\text{solution}} = P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}} \quad \dots\dots\dots(\text{Equation 05})$$

4.0 RESULTS AND DISCUSSION

It is clear that the reduction of evaporation rate is greatly influenced by dissolved salts. Evaporation rate directly depend on relative difference between the equilibrium vapour pressure of the liquid and the partial vapour pressure of the liquid in air. The vapour pressure of an aqueous solution reduces due to dissolved salts. Salt solution has a lower equilibrium vapour pressure than the pure water at the same temperature. This vapor pressure reduction of solution is described under the colligative properties of solution (Atkins, 1998). Figure 1 shows the deviation of evaporation

pattern of individual salt solutions and Dead Sea water from pure water. Understanding and accounting evaporation pattern deviation due to dissolving salts in pure water is essential in development of evaporation models for saline water bodies such as the Dead Sea.

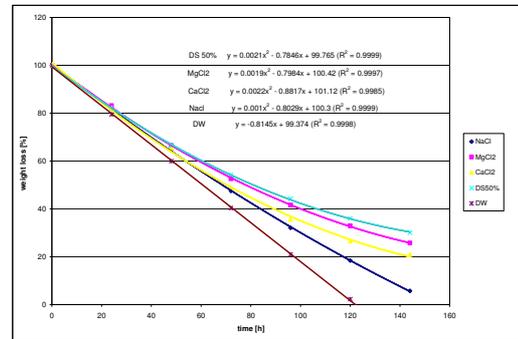
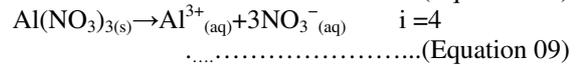
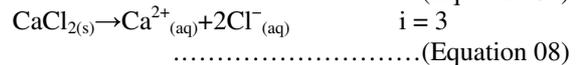
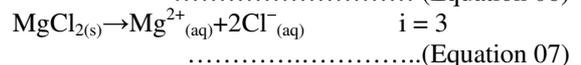
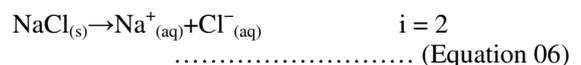


Figure 1: Relationship between percentage weights remaining with time, comparing distilled water and electrolyte solutions

Evaporation rate of salts solutions is lower than distilled water (DW) due to dissolved ions effect (Figure 1). DW shows a linear relationship while all other salt solutions show a polynomial relationship, because the evaporation rate decreases with concentration. In salt solution, evaporation removes only water and dissolved ions remain in the solution. Therefore, total number of moles automatically increases with evaporation over time.

In electrolyte solutions, colligative properties of solution depend on number of solute particles, but not on their nature. Therefore, it is important to consider the composition of salts. Different salts give different number of ions depending on ionic composition when salt dissolves in water. For example, a single NaCl molecule dissociate into two ion particles (Equation 06) in water, one molecule of MgCl₂ or CaCl₂ dissolve and give three ion particles (Equations 07 and 08), and Al(NO₃)₃ dissociates into four ion particles (Equation 09) when making the ionic solution, where i value is the number of particles into which the solute dissociates



According to the results that were obtained by experiment, 1:3 electrolyte solution (Al(NO₃)₃) shows the minimum tendency to evaporate while 1:1 electrolyte (eg- NaCl) shows the maximum tendency to evaporate, and 1:2 electrolytes (e.g.-

MgCl₂ , CaCl₂) show medium tendency to evaporate (Figure 01).

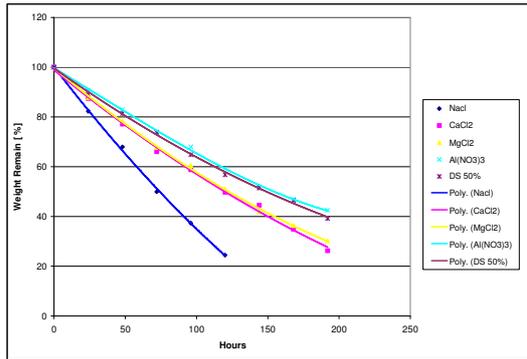


Figure 2: Percentage weight of ionic solution remaining in beaker during evaporation test

The weight loss rate represents effective evaporation rate (evaporation of water expressed as height reduction per unit time). In Figure 2, slope of curves indirectly represent the evaporation rate of each liquid. According to Figure 2, NaCl has the highest slope while Al(NO₃)₃ has the lowest slope, and CaCl₂ and MgCl₂ have intermediate slopes. Slope of the CaCl₂ and MgCl₂ curves show almost equal values because both electrolytes have the same number of ions. Interestingly, Dead Sea solution gives a slope that is higher than the slope of 1:2 electrolytes and less than 1:3 electrolytes. This can be due to high concentration of total ion in Dead Sea water sample. Dead Sea consists of different type of salts which affect the concentration of ions differently. Since the Dead Sea water is a mixture of ionic compound, evaporation depends on activity of water that is affected by the different dissolved ions and not the salts (Martin, 1983). Some dissociate into less number of ions and some more when dissolve as discussed earlier. Therefore, it is important to talk about the variety of the ionic compounds and their concentrations as well when it comes to discuss about the evaporation rate.

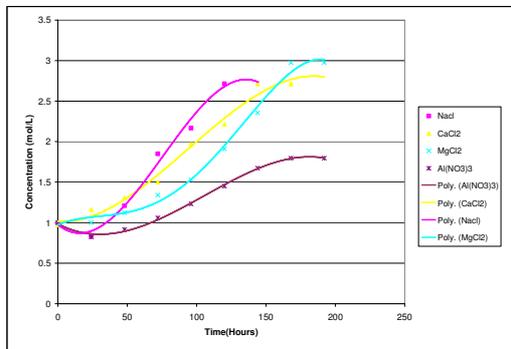


Figure 3: Changing the concentration of electrolyte solutions during evaporation test

Concentration increases with time until saturation. When saturation point is reached, concentration remains constant and precipitation

occurs. Best fitted curve until saturation is generated by a 3rd order polynomial relationship since concentration increases in decreasing rate and reaches a constant at around saturation.

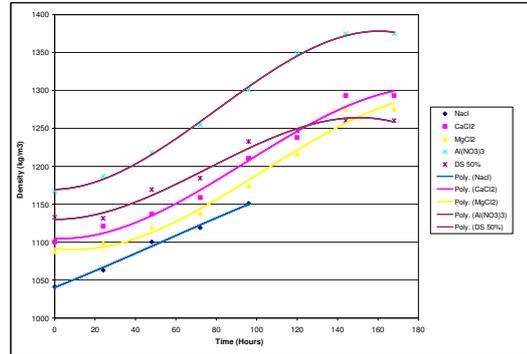


Figure 4: Change in density of salt solutions during evaporation

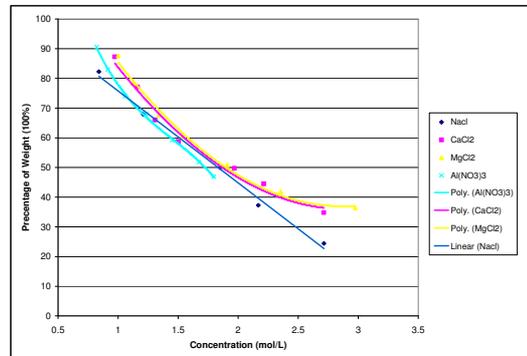


Figure 5: Relationship between concentration of ionic solutions and percentage of weight of solution during the evaporation process

In Figures 3 and 4, during the evaporation process, concentration and density increases with time since only the water molecules evaporate and salts remain in the solution. It is clear and common to all solutions that evaporation reduces with the increasing concentration (Figure 5). In low number electrolytes (NaCl, CaCl₂, MgCl₂), effective evaporation rate is high. Therefore, a higher concentration is achieved quickly than a higher number electrolyte (Al(NO₃)₃). In higher concentration, water molecules have low tendency to evaporate. The evaporation rate (slope of curves in Figure 2) reduces with concentration. Therefore, reduction rate of the slope is higher in a low number electrolyte. In other words, low number electrolyte reaches a constant evaporation rate quickly compared to higher number electrolytes in this experiment. At saturation, precipitation can be observed and concentration does not change further. By comparing Figures 3 and 4 with Figure 5, two stages that are before precipitation and after precipitation stages can clearly be identified.

The minimum evaporation rate can be observed at the saturation concentration. After reaching the saturation point, precipitation can be observed and

evaporation process continues at minimum evaporation. The evaporation rate never reaches zero.

All the curve fittings were done statistically. Regression analysis was done for the data set that separated before precipitation of salt. Regression analysis of concentration and weight loss percentage provides useful information about the evaporation rate of different ionic solutions. Regression curve equations are displayed in table 1. All relationship models have a co-relation of determination (R^2) that is greater than 95%. Therefore, relationships can be considered as reliable relationships, and functions describe the relationship between concentration and weight percentage of remaining solution.

Electrolyte	Regression Equation	R^2
NaCl	$y = -32.792x + 109.09$	99.5%
Ca Cl ₂	$y = 13.338x^2 - 77.146x + 147.53$	98.0%
Mg Cl ₂	$y = 13.83x^2 - 79.462x + 151.05$	99.3%
Al(NO ₃) ₃	$y = -43.613x^3 + 189.43x^2 - 306.05x + 238.05$	99.9%

Table 1: Regression curve equations and correlation

First derivative of above equations give the slope of curves which express the evaporation rate (Table 2).

Electrolyteslope	Validity
NaCl $dy/dx = -32.79$	$x < 2.9$
Ca Cl ₂ $dy/dt = 26.83x - 77.146$	$x < 2.9$
Mg Cl ₂ $dy/dt = 27.66x - 79.462$	$x < 2.8$
Al (NO ₃) ₃ $dy/dt = -130.84x^2 + 378.86x - 306.05$	$x < 1.7$

Table 2: Slopes of regression curves

Concentration, x , is valid until the saturation concentration (point where the salt precipitation is first visible). The evaporation of 1:1 electrolyte is described from a linear function of concentration. The evaporation of 1:2 electrolytes is described by a 2nd order polynomial function of concentration, and the evaporation of 1:3 electrolytes is described by a 3rd order polynomial function.

5.0 CONCLUSION

As the colligative properties of salt solution, Dead Sea evaporation rate is significantly lower than fresh water. Dissolved ion in Dead Sea water reduces the vapour pressure of water. Depending on number of ions dissolved in water of each salt,

vapour pressure of solution changes. Therefore, evaporation rate of Dead Sea is determined by its composition. Increasing concentration of each dissolve salt in Dead Sea water reduce the magnitude of vapour pressure according to Raoult's law.

According to two models that is mentioned by Asmar and Ergenzinger in 1999, the evaporation rate becomes zero when salinity reaches a certain salinity level (483.55g/L model is based on Dalton-type formula, 486.2 g/L is model based on modified Penman's method). Based on the two models, they describe that there is no evaporation after salinity level reaches around 485g/L and the Dead Sea level cannot drop further due to evaporation. But according to results we obtained, it is impossible for the evaporation rate to drops to zero. After a certain level of salinity is reached, the evaporation rate drops to its minimum, which is a constant value which does not decrease further.

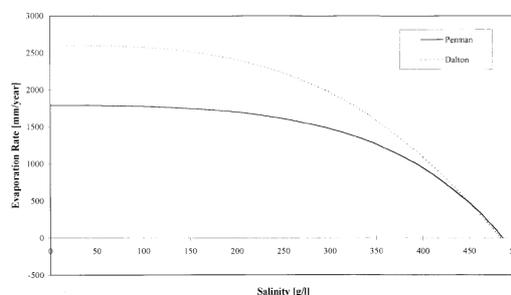


Figure 3: Effect of salinity on the yearly evaporation rate (Asmar and Ergenzinger, 1999)

Finally, when developing a model for measurement of evaporation in the Dead Sea, collective effect of different dissolved ions should be accounted.

6.0 REFERENCES

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