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Evaluation of salt effects on some thermodynamic properties of Urmia Lake water

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ABSTRACT: In this study some thermodynamic parameters including freezing point, boiling point and the vapor pressure of Urmia Lake salt water were investigated as some important environmentally monitored physicochemical properties of Urmia Lake. In this regard salt concentration is chiefly responsible for the modification of the thermodynamic properties of Urmia Lake water which affects its overall environmental and ecological characteristics. On the other hand, the Urmia Lake is now supposed to be the most convenient place for many rare aquatic species and therefore interpreted to be unique from the viewpoint of qualitative characteristics. For the goals of this study water sampling and analysis where performed in two wet and dry periods of the lake in order to represent the extremes of the lake's environmental variability. Prevailing chemical ions in the water body were determined and used for the estimation of the relative thermodynamic coefficients of salt water for the acquisition of the freezing point, boiling point and the vapor pressure of the Urmia Lake water. Interpolated calibration curves were plotted for the changes in the studied parameters versus a variety of salt concentrations indicating a linear relationship between the investigated parameters and the prevailing salt concentration of the Urmia Lake. The calibration curves were then formulated to simplify the estimation of the thermodynamic parameters of the Urmia Lake for any salinity conditions. Real sample analysis also showed a very good agreement between the estimated and observed values.

Key words: Urmia Lake, Salt water, Freezing point depression, Boiling point elevation, Vapor pressure deficit,Calibrated equations

INTRODUCTION

The quality of surface water within a region is governed by both natural and anthropogenic effects (Aljuboury, 2009, Baghvand *et al.,* 2010, Uba *et al.,* 2009, Dauvalter *et al.,* 2009, Vasanthavigar *et al.,* 2009, Nasrabadi *et al.,* 2009, Mahavi *et al.,* 2005, Nasrabadi *et al.,*2010, Nouri *et al.,* 2008, Nabi Bidhendi *et al.,* 2007, Pejman *et al.,* 2009, Kazi *et al.,* 2009,). Urmia Lake is the 20th largest lake in the world by area and the second most hyper saline lake. This lake is located in the province of Azerbaijan, northern west part of Iran (Karbassi *et al.,* 2010). The lake has an area of about 5500 km^2 and encompasses 50 small islands (Fazeli *et al.,* 2006). Mean annual temperature and precipitation in the area are 11.2 °C and 341 mm, respectively, while mean maximum and minimum temperatures occur in July (23.9°C) and January (-2.5°C), respectively (Djamali *et al.,* 2008). About 30 small and large rivers flow into the lake (Karbassi *et al.,* 2010). These rivers with a mean annual inflow of about 4.6 billion cubic meter are the principal origins of water to the lake (Zeinoddini *et al.,* 2009). Urmis Lake is now supposed to be the most convenient place for many rare aquatic species such as *Artemia* in the world (Fazeli *et al.,* 2005).

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Investigating about thermodynamics properties such as freezing point, boiling point, vapor pressure and etc., from saline solutions is important for designing, constructing and operating saline and hypersaline shallow lakes for mineral extraction and energy production (Turk, 1970, Oroud, 1994, Ahmadzadeh kokya, 2008). The dissolved salts lower the free energy of the water molecules, causing a decrease in the vapour pressure above the lake, and, as a result, causing a decrease in the evaporation rate from such lakes compared with freshwater lakes with the same conditions apart from salinity (Asmar, 1999). Several investigators such as Meyer (1915), Penman (1948), Marciano and Harbeck (1952) proposed several equations relating salt water thermodynamic properties to the hydrological parameters on the basis of large amounts of experimental data. Other researchers have mainly focused on water thermodynamic properties (Zhiqing et al. 1987, Hunter 1983, Featherstone and O'Grady, 1997, Winzor, 2004, Ouyang, 2005, Lee *et al.,* 2008, Karbassi *et al.,* 2008, Stanhill, (1994), Asmar and Ergenzinger (1999), Chow 1964, Chow *et al.,* 1988, Alizadeh, 1996, Lide, 2004, Valiantzas, 2006, Lychnos *et al.,* 2010), acquiring experimental formulations. In this respect El-Dessouky et al. (2002) showed that a decrease in the evaporation rate upon an increase of the water salinity because of the reduction in the water vapor pressure at the water surface. Oroud (1999) found that there is a logical relationship between temperature and evaporation dynamics of saline solutions. He could drive a quantitative assessment of the sensitivity of temperature and evaporation owing to changes in the activity coefficient of a saline solution. Ali et al. (2001) were successful introducing a parameter as the reduction factor due to salinity for the surface to open air vapor pressure difference. The latter was being reformed utilizing the vapor pressure deficit for the estimation of evaporation rate from salt water resources (Ahmadzadeh *et al.,* 2008). This has encouraged us to evaluate the effects of saline water concentration on some thermodynamic properties of Urmia Lake water. On the other hand, the Urmia Lake has recently encountered a dry period in which the water balance of the lake is negative and therefore the water loss imposed a critical condition to the water chemical quality (Ahmadzadeh, 2006). The main objective of this study was to evaluate a more accurate estimation for the relative coefficients of the effects of salt concentration of a water body on the boiling point elevation, freezing point depression and water vapor pressure deficit. For obtaining this purpose, physicochemical quality and hydrochemistry of salt water were evaluated in two wet and dry periods of the lake in order to represent the extremes of the lake's environmental variability. To ensure accuracy, the calculated values were calibrated, interpolated and compared using practical observations simultaneously.

MATERIALS & METHODS

Reagents and Apparatus

All water samples studied in this study were directly prepared from the Urmia Lake. Solutions of lower concentrations were prepared daily by a suitable dilution of the Urmia Lake salt water. Sampling and sample preparation was performed according to Pawliszyn (2002). All tests were carried out as quickly as possible at the local stations nearby the Urmia Lake to take the advantage of the same meteorological conditions.

A SAMSUNG refrigerator (Model SR-L727EV) was used for freezing and a HACH heater (Model 240vac) was used for boiling purposes. A HACH digital thermometer (Model 4445001) was used for temperature logging throughout the experiments. A Portable WTW Multi-meter (Model Profiline 197i) was used for the determination of the electrical conductivity (EC) and total dissolved solids (TDS). Other data were acquired from the national meteorological organization (IMO, 2010).

One of the most succinct ways in presenting the changes of state that water can undergo is in terms of its phase diagram. A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state. The temperature at which, under a specific pressure, the liquid and solid phases of a substance coexist in equilibrium is called freezing point. Respectively, the temperature, at which the vapor pressure of a liquid is equal to the external pressure, is called boiling point (Atkins, 1999).

For the estimation of the boiling and freezing temperatures of Urmia Lake water, the colligative properties of water versus the concentration of chemical salts were investigated. All the colligative properties stem from the reduction of the chemical potential of a liquid solvent as a result of the presence of solute and the increase in disorder. The reduction in chemical potential of solvent implies that the liquid-vapor equilibrium occurs at a higher temperature and the solid-liquid equilibrium occurs at a lower temperature (Atkins, 1999). As a logical result the boiling point of salt water elevates to higher degrees and its freezing depresses to lower degrees as well as the reduction of the vapor pressure of the solution in comparison with the pure water (eq. 1a & 1b).

$$\Delta T_b = iC_m k_b \qquad (eq.1a)$$

$$\Delta T_f = iC_m k_f \qquad (eq.1b)$$

where ΔT_b (K) and ΔT_f (K) are subsequently the changes in boiling and freezing points, i(1.8) is Van't Hoff coefficient, C_m is molality defined as moles per kg of water (Licker, 2003), k_b *(0.512 K kg mol*$^{-1}$*)* and k_f*(-1.86 K kg mol*$^{-1}$*)* are subsequently ebullioscopic and cryoscopic constants of water.

Alternatively, the effect of salinity is to reduce the vapor pressure of salt water but at the same time to increase the energy returned to the atmosphere by other physical processes, so that under equilibrium conditions a saline solution reaches a temperature higher than that of pure water (Harbeck, 1955). This reduction stems from the increase in ion activity and the reduction of thermodynamically spontaneous change of a liquid phase into a vapor phase (Atkins, 1999). In this way, the vapor pressure of salt water can be linked to the salinity by introducing water molar fraction, as an effective variable in a salt solution (Ahmadzadeh, 2008). In this regard the multiplication of the molar fraction of salt water to the vapor pressure of fresh water yields the vapor pressure of salt water (eq. 2a & 2b).

$$P_{H_2O} = P^0_{H_2O} X_{H_2O} \qquad (eq.2a)$$

$$\Delta P = P^0_{H_2O}(1 - X_{H_2O}) \qquad (eq.2b)$$

Where ΔP is the vapor pressure deficit, P_{H_2O} is the water vapor pressure above a salt water solution and $P^0_{H_2O}$ is the standard water vapor pressure above fresh water and X_{H_2O} is the water molar fraction.

RESULTS & DISCUSSION

The prevailing dissolved salt in Urmia Lake water is NaCl which is the main responsible for the chemical characteristics of the Urmia Lake water (Ahmadzadeh, 2008). Therefore most of the mentioned thermodynamic constants in equations 1 and 2 are related to the NaCl water solution. On the other hand, the Urmia Lake undergoes two wet and dry periods in a year in which the salt concentration alternates dramatically. In this regard the changes of studied parameters were calculated using the actual conditions in both wet and dry periods (Table 1). The calculated values showed that the shift in the boiling and freezing points as well as the vapor pressure of Urmia Lake water is more intensive in dry period than that of wet period (Table 1). As a result the phase diagrams of Urmia Lake water were generated for both of climatological conditions of the lake (Fig. 1 & 2).

Data validation and real sample analysis

According to the calculated deficit values for some thermodynamic parameters and further application of equations 1 and 2, for various probable salt water concentrations, calibrated diagrams for the changes of boiling and freezing points as well as vapor pressure deficit were plotted versus TDS value of water (Fig. 3 & 4). These diagrams enables the determination of the changing values of the freezing point, boiling point and the vapor pressure of Urmia Lake water for a variety of salinity conditions, e.g. wet and dry periods. Satisfactory linearity of the acquired calibration curves with the correlation coefficient of 0.99 is logically capable of reforming the eq. 1a & 1b to eq. 3a & 3b:

$$\Delta T_b = 0.017 TDS - 0.103 \qquad (eq.3a)$$

$$\Delta T_f = -0.061 TDS + 0.361 \qquad (eq.3b)$$

Alternatively, the vapor pressure of Urmia Lake may be expressed with the modified version of eq. 2a & 2b, as follows (eq. 4a & 4b):

$$\Delta P / P^0_{H_2O} = 0.0006 TDS + 0.0046 \qquad (eq.4a)$$

$$\Delta P = P^0_{H_2O}(0.0006 TDS + 0.0046) \qquad (eq.4b)$$

In order to assess the accuracy of modified equations, sampling was performed in two campaigns during wet and dry periods of Urmia Lake. In each campaign three samples were gathered and analyzed for the practical determination of freezing point, boiling point and vapor pressure. Results indicated no significant difference from that of estimated values. Maximum error barely exceeded 2% for the studied parameters (Table 2).

CONCLUSION

According to the results, Sodium chloride was found to be the Prevailing chemical salt in the Urmia Lake water. Therefore the estimation of the thermodynamic coefficients and further acquisition of the freezing point, boiling point and the vapor pressure were performed according to its thermodynamic reactivity. Interpolation of the calibration curves led to define modified formulations for the studied parameters for the case of Urmia Lake water body. Results showed that on the extremes of the Urmia Lake salinity conditions, the boiling point may undergo an elevation of about 5.1 °K in dry period and 2.7 °K in

Table 1. Experimental Data for Urmia Lake water

Parameter	Wet period	Dry period
Total dissolved solids (TDS)	177 g L^{-1}	324 g L^{-1}
Salt concentration (C_m)	3.07 mol kg^{-1}	5.57 mol kg^{-1}
Van't Hoff's coefficient (i)	1.8	1.8
Ebullioscopic constant (k_b)	0.512 K kg mol^{-1}	0.512 K kg mol^{-1}
Cryoscopic constant (k_f)	-1.86 K kg mol^{-1}	-1.86 K kg mol^{-1}
Standard vapor pressure (P^0_{H2O})	23.32 mmHg	24.21 mmHg
Calculated values	***Wet period***	***Dry period***
Boiling point elevation (ΔT_b)	+2.73 K	+5.08 K
Freezing point depression (ΔT_f)	-10.44 K	-20.12 K
Vapor pressure deficit (Δp)	2.35 mmHg	5.19 mmHg

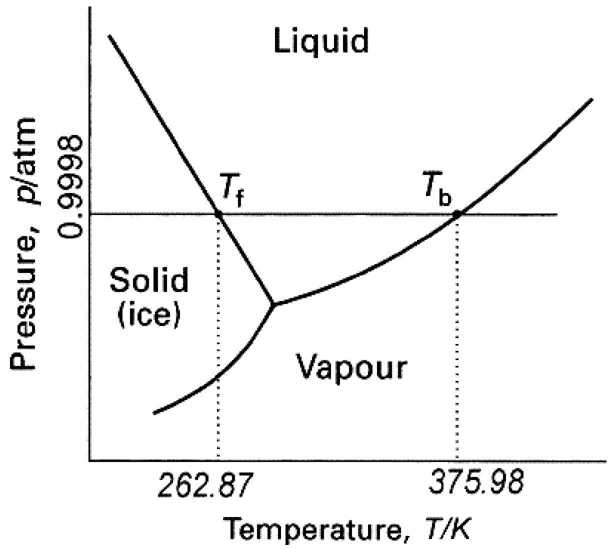

Fig. 1. Phase diagrams of Urmia Lake water in wet and dry periods

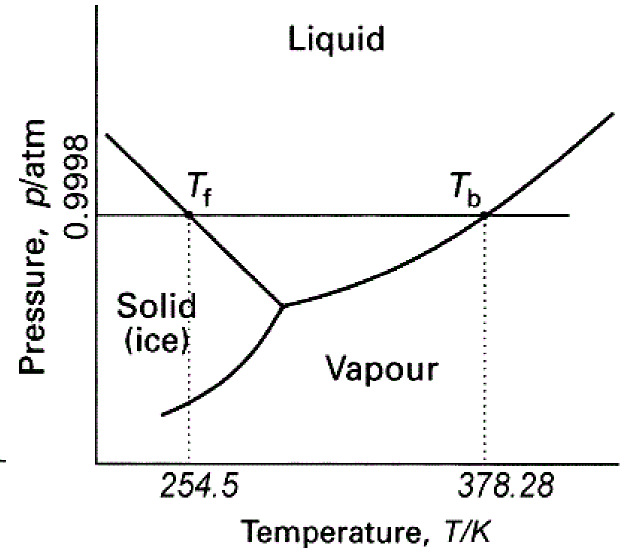

Fig. 2. Phase diagrams of Urmia Lake water in wet and dry periods

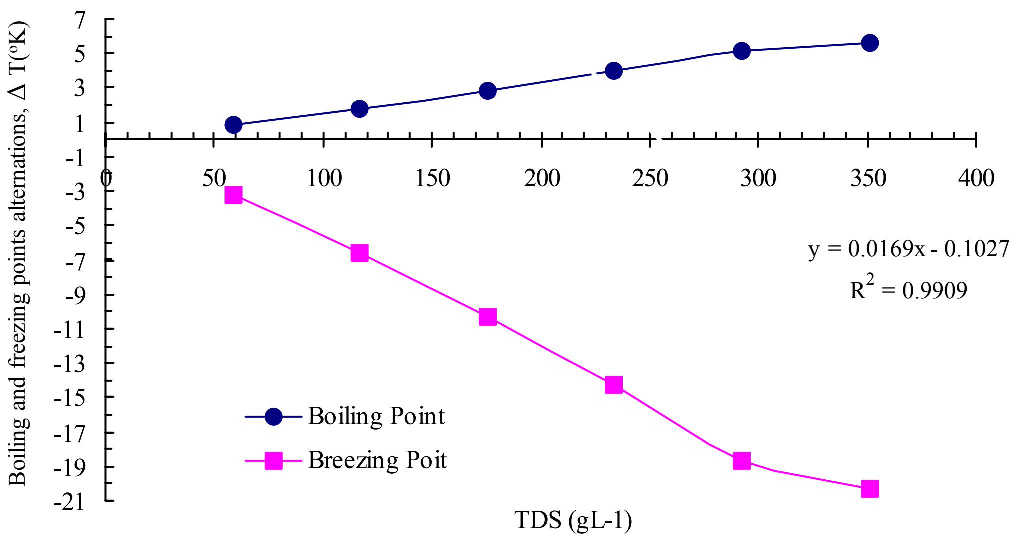

Fig. 3. Calibration curves of the changes of boiling and freezing points versus TDS

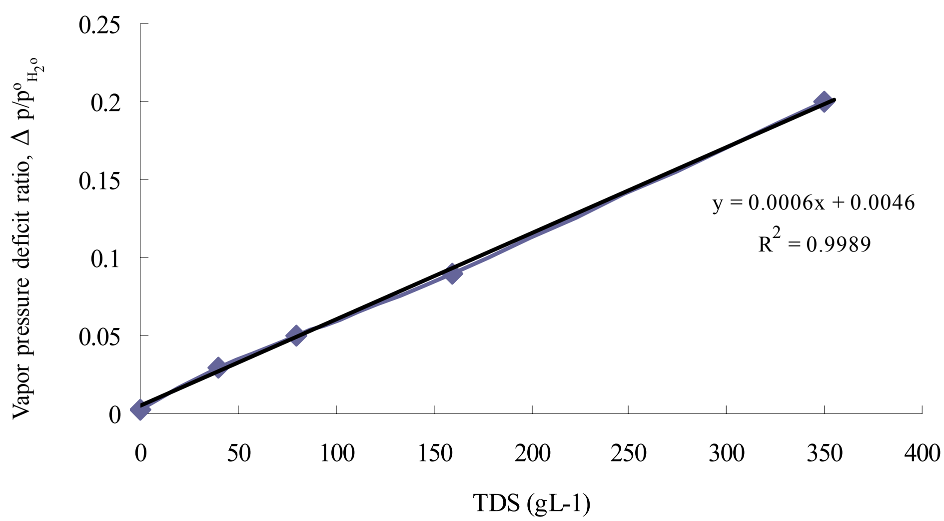

Fig. 4. Calibration curve of the vapor pressure deficit versus TDS

Table 2. Comparison list of real sample analysis versus the calculated values

Parameter[a]	Wet period	Error	Dry period	Error
Calculated boiling point	375.88 K	0.1 %	378.23K	0.2 %
Observed boiling point	376.3 K		379.1 K	
Calculated freezing point	262.71 K	0.3 %	253.03 K	0.2 %
Observed freezing point	261.9 K		253.6 K	
Calculated vapor pressure	20.97 mmHg	1.2 %	19.02 mmHg	1.8 %
Observed vapor pressure	21.22 mmHg		19.37 mmHg	

[a] All the experiments were performed at 0.9998 atm, nearby the Urmia Lake

wet period, while the freezing point shows a maximum depression of 20.1 °K and 10.5 °K for dry and wet periods respectively. Meanwhile, water vapor pressure undergoes an overall deficit of 5.2 mmHg and 2.4 mmHg respectively. Thus, the Urmia Lake salt water exists in a wider extension of temperature in comparison of fresh water, due to the boiling point elevation and freezing point depression as well as vapor pressure deficit which reduces the evaporation rate.

Real sample analysis showed a very good agreement between estimated and observed values. The calibration curves were also formulated based on the equations 1 & 2, in order to simplify the estimation of the studied parameters for any salinity conditions of the Urmia Lake. The results showed that how the salt concentration could affect the physicochemical characteristics of the Urmia Lake to be a unique and suitable settlement for some rare aquatic species.

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