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Thermochemistry of Natural Hypersaline Water Systems Using the Urmia lake as a Case

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In order to study the heat effect of mixing of fresh waters (winter rains in the form of floods) with Urmia lake water , the heats of mixing of Urmia lake water with distilled water at 25°C have been measured. On the basis of these experimental data, the heats of dilution of freshwater in Urmia lake water and Urmia lake water in fresh water have been calculated. By considering the isothermal cycle of the dilution of Urmia lake water, the partial heat of evaporation of water from Urmia Lake water was found to be ca. 2443.58 $kJ.(kg\ H_2O)^{-1}$ at 25°C.

Keywords: Heat of mixing; partial heat of evaporation; *Urmia lake* water; Dilution; natural hyper saline brines.

1. Introduction

Lake Urmia (or Orumiyeh), is one of the largest permanent hypersaline lakes in the world and resembles the Great Salt Lake in the western USA in many respects of morphology, chemistry and sediments (Kelts *et al.* 1986). Despite this, and its several values, including conservation, little literature has been published on the lake and its biota (Jalali 1984, Van Stappen *et al.* 2001, Eimanifar *et al.* 2005, Eimanifar *et al.* 2006, Asadpor *et al.* 2007, Anon 1987)

Urmia Lake with an ionic strength between 6.5-7.5, located in north western Iran at an altitude of 1275 m above sea level. The total surface area ranges between 4750 km2 and 6100 km^2 (Azari *et al.* 1987) depending on evaporation and water influx. The air temperature usually ranges between 0 and -20°C in winter, and up to 35°C in summer (Anon 1991). From this point of view, Urmia lake is a critical asset for the region, because it acts to moderate these extremes (Street-Perrott *et al.* 1983).

The main cations in the lake water include Na^+, K^+, Ca^{2+}, and Mg^{2+}, while Cl^-, SO_4^{2-}, HCO_3^- are the main anions (Touloie 1998). Sodium ions are at slightly higher concentration in the south compared to the north of the lake, which could result from the shallower depth in the south, and a higher net evaporation rate (Komili Birjandi 1999, Baveghar *et al.* 1998).

Hydrologic conditions are extremely important for the maintenance of a natural brine body's structure and function and affect many abiotic factors which, in turn, may impact the biota that develop in it (Mitsch *et al.* 2000). Because saline lakes occur primarily in endorheic basins, they may be particularly sensitive to environmental changes because their size, salinity and annual mixing regimes vary with alterations in their hydrologic budgets (Jelison *et al.* 1998, Romero *et al.* 1996).

All physical and chemical phenomena in natural brine bodies are accompanied by thermal effects, which may have considerable practical and theoretical importance. Two examples of such effects are heat of dilution and heat of evaporation. The heat of dilution of natural brine by fresh water originating from floods and rains may cause local heat effects where the phenomenon occurs, and its influence on some physicochemical properties and chemical processes in a particular area can be very significant. The heat of evaporation of water from natural brines is also a very important parameter for calculating the evaporation rate, which can permit some estimates concerning the mechanism of formation of natural evaporatives. In the present work, we will consider the Urmia lake as an example of a natural hypersaline brine and discuss the measurement of its heat of dilution by fresh water and the heat of evaporation of water from it.

There are several methods for the calculation of the partial heat of evaporation $\Delta\overline{H}_{evap}$. One of them is based on the Clapeyron equation and uses vapor pressure data at various temperatures

$$\Delta\overline{H}_{evap} = \Delta\overline{V}_1 T\left(\frac{dP}{dT}\right) \tag{1}$$

where T is the Kelvin temperature, $\Delta\overline{V}_1$ is the change in partial volume of one mole of water when it evaporates from a liquid solution to the vapor phase; $\left(\frac{dP}{dT}\right)$ is the first derivative of the temperature dependence of the vapor pressure of a particular solution at a given temperature T. For the process of water evaporation from the Urmia lake, the $\Delta\overline{V}_1$ values are the difference between the molal volume of saturated vapor V_{sat} over Urmia lake water, and the partial molal volume $\Delta\overline{V}_1$ of water in Urmia lake water, which can be calculated from the density data of mixtures of water and Urmia lake water. The V_{sat} can be found as the volume of superheated steam at a given temperature T and vapor pressure P_i over the Urmia lake.

The use of the partial functions $\Delta\overline{\mathrm{H}}_{evap}$, $\Delta\overline{V}_1$ and $\overline{V}_1$ in Eq. (1) is explained by the fact that the evaporation process is considered to be under such thermodynamic conditions that the evaporation of one water mole from a solution to the vapor phase does not lead to a change of solution concentration. To use Eq. (1) for the calculation of the partial heat evaporation of water from the Urmia lake, we need the temperature dependence of the vapor pressure over Urmia lake water, which is lacking now.

Another method for the calculation of the partial heat of water evaporation from a natural brine can be based on the use of the heat of dilution of this brine by fresh water. Let us consider the isothermal cycle of the dilution of Urmia lake water by two ways: a) by the addition of one mole of liquid fresh water to Urmia lake water; and b) by the evaporation of one mole of fresh water and by the addition of the obtained steam to Urmia lake water. Both processes must be carried out under the condition that the alteration of the solution concentration, after the addition of the considered amount of solvent, will be negligible.

Under such conditions, the obtained thermodynamic functions are partial ones. The discussed cycle is given in Fig. 1.

The symbols used in this cycle are as follows:

1. P_0 and P_i are the vapor pressure over pure water and over Urmia lake water , respectively, at the given temperature;

2. H' is the enthalpy of the water at the given temperature and a pressure equal P_0

3. $H_{\sup}$ is the enthalpy of superheated water steam at the given temperature and a pressure equal P_i

4. H_1° is the enthalpy of pure water at the given temperature

5. $\overline{H_1}$ is the partial enthalpy of water in a particular solution (in our case- Urmia lake water) at the given temperature

According to the thermodynamic definition

$$\Delta\overline{H}_{evap} = H_{\sup} - \overline{H}_1 \tag{2}$$

and

$$\overline{L}_1 = \overline{H}_1 - H_1^0 \tag{3}$$

where $\overline{L}_1$ is the partial heat of dilution.

Considering the above-discussed thermodynamic cycle, we can write:

$$(H' - H_1^0) + (H_{\sup} - H') + (-\Delta\overline{H}_{evap}) = \overline{L}_1$$

and finally:

$$\Delta\overline{H}_{evap} = -\overline{L}_1 + (H_{\sup} - H_1^0) \tag{4}$$

Equation (4) can be used for the calculation of the partial heat of water evaporation from Urmia lake water. The values of $H_{\sup}$ and H_1^0 can be taken from any tables of the thermodynamic properties of water and water vapor, but the heat of dilution should be experimentally measured. The study of the heat of dilution of Urmia lake water by fresh waters is important not only for $\Delta\overline{\mathrm{H}}_{evap}$ calculation. Every year during the winter and spring months we encounter the phenomenon when rain waters in the form of floods are mixed with Urmia lake waters. During this process, some thermal effects also take place.

2. Experimental

The heats of mixing of Urmia lake water with distilled water ΔH_{mix} have been measured on a thermoanalyse microcalorimeter VP-ITC type. At the first, the concentration of ions in Urmia lake water has been measured.

Before injection of sample, distilled water Microcalorimeter apparatus, sample and distilled water are poured to separate cells and for five minute enter to the Thermo Vac that has degassing. 1.5 ml of Urmia lake water was inject with syringe to sample cell and the same amount of deionized water was injected to reference cell in Microcalorimeter. Distilled water with the help of auto-pipette in the time internal has been injected to the working cell. The volume of auto-pipette is 300 μL .

The entire ΔH_{mix} curve (Fig. 2) was obtained by adding Urmia lake water to distilled water and (Fig. 3) was obtained by adding distilled water to Urmia lake water. In the first case, distilled water was supplied to the bottom of the working cell with Urmia lake water. In the second case, Urmia lake water was supplied to the consecutive addition method was used.

When heavy Urmia lake water was added to the cell with fresh water, the supply of Urmia lake water was under constant stirring in order to prevent the formation of two layers.

The ionic concentrations (in molality units) of the Urmia lake water used for mixing experiments were as follows:

Sodium and potassium ion concentrations were determined using a flame photometer with a precision of ±0.2%. Calcium ion concentrations were found with an accuracy of ±0.25% by complexometric titration with $EDTA$, described by Krumgalz and Holzer[25]. The total content of calcium and magnesium ions was determined by complexometric titration with $EDTA$. The magnesium ion content was then calculated as the difference between the total magnesium and calcium ionic content and the calcium ion concentration found by separate titrations. The sulfate anion concentration was determined by the conventional spectrophotometer method with $BaCl_2$. The total content of chloride anions was found with an accuracy of ±0.1% by argentometric titration.

3. Conclusion

All experimental results of ΔH_{mix} measurements at 25ºC are presented in Tables II and III. The values presented in these tables have been calculated using the following equation

$$G_{total} = g_{ULW} + g_{H2O} \tag{5}$$

where g_{UlW} , and g_{H2O} are the amounts of Urmia lake water and bidistilled water, respectively, taken for the experiment, and G_{total} is the total weight of the mixture formed. The values Δg_{ULW} and Δg_{H2O} are the amounts of the appropriate water added in the cases of the consecutive addition procedure.

$$r_W = \frac{g_{ULW}}{G_{total}} \tag{6}$$

Here, r_W is the weight fraction of Urmia lake water in the particular mixture obtained.

$$I_m = (\frac{1}{2})\sum_i m_i Z_i^2 \tag{7}$$

I_m is the ionic strength (in molality units) of the particular mixture formed and m_i and z_i are the molality and charge of an ion (i), respectively. The ionic concentrations of every mixture have been calculated using the ionic concentrations of Urmia lake water and its weight fractions in the mixtures.

$$\Delta H_{mix} = \frac{\Delta Q}{G_{total}} \tag{8}$$

ΔQ is the heat effect of the one-step mixing for the particular amount of the mixture. For the consecutive addition procedure, the total heat effect ΔQ_i on a particular step (i) will be equal to

$$\Delta Q_i = \Delta Q_{i-1} + \Delta(\Delta Q)_i \tag{9}$$

where ΔQ_{i-1} is the total heat effect for the previous step and $\Delta(\Delta Q)_i$ is the heat effect obtained for the i^{ih} particular addition .

The ΔH_{mix} values for the mixing of Urmia lake water with bidistilled water at 25°C over the entire range of r_W values from 0 to 0.5 have been measured by two procedures, namely by consecutive addition of Urmia lake water to bidistilled water (Fig. 2) and by consecutive addition of H_2O to Urmia lake water (Fig, 3). Both curves in Fig. 2, 3 are exothermic and show little asymmetry with maxima placed near I_m = 8 (for fresh waters to the Urmia lake waters) and I_m =3 (for Urmia lake water to the fresh waters).

In these experiments, two sorts of thermal effects have been obtained:

1. the heat of solution (dilution) L_1 of fresh water in Urmia lake water

$$L_1 = \frac{\Delta Q}{g_{H2O}} \tag{10}$$

2. the heat of solution (dilution) L_2 of Urmia lake in fresh water

$$L_2 = \frac{\Delta Q}{g_{ULW}} \tag{11}$$

The values L_1 and L_2 are presented in the last columns in Tables II and III and in Figs. 4 and 5.

As seen from these figures:

1. The L_2 values are proportional to the weight fraction of Urmia lake water in the formed mixtures with $r_W < 0.0685$ and the limiting value of L_2 at infinite dilution L_2^0 is equal to -0.938 $kJ.(kg\ ULW)^{-1}$.
2. The curve $L_2 = f(r_W)$ has a strong inflection point at $r_w \sim 0.0075$ which can indicate strong structural changes in the formed mixtures.
3. The extrapolation of the relationship of $L_1 = f(r_W)$, Heat of dilution of water in Urmia lake water as a function of the weight fraction of water, to $r_W = 0.5$ gives the $\overline{L_1^\circ}$ (the limiting partial heat of the dilution of water in Urmia lake water) equal to about -3.6 $kJ.(kg\ H_2O)^{-1}$. This value can now be used for the estimation of the partial heat of evaporation of water from Urmia lake water $(\Delta\overline{H}_{evap})$.

For the calculation of the heat of evaporation of water from Urmia lake water (ΔH_{evap}^0) at 25ºC by Eq. (4), we used $\overline{L_1^\circ}$ = -3.6 $kJ.(kg\ H_2O)^{-1}$, found above, and the known values (Handbook of Chemistry and Physics, 1982) of $H_{\sup}$ = 2544.71 $kJ.(kg\ H_2O)^{-1}$ and H_1^0 = 104.73 $kJ.(kg\ H_2O)^{-1}$.

Then using Eq. (4) we obtain:

$$\Delta\overline{H}_{evap}^0 = -(-3.6) + (2544.71 - 104.73) = 2443.58 \quad kJ.(kg\ H_2O)^{-1}$$

We feel that this value has a reasonable meaning compared to other electrolyte solutions having similar concentrations, as calculated by Mashovets *et al*. (1965). Independent checking of the $\Delta\overline{H}^{0}_{evap}$ value will be done after the experimental measurements of the temperature dependence of vapor pressure over Urmia lake water is available.

References:

Anon : A study report on natural lakes of Azarbayjan Province. Ministry of Energy, Tehran 1987.

Anon : A study for the establishment of natural park on the islands of Urmia Lake. Environment protection Bureau of West Azarbayjan province Tehran 1991, 1-3.

Asadpour Y, Motallebi A, Eimanifar A: Biotechnological approach to produce chitin and chitosan from the shells of Artemia urmiana Gunther, 1899 (Branchiopoda, Anostraca) cysts in Urmia Lake, Iran. Crustaceana 2007, 80(2):171-180.

Azari Takami G: The use of Artemia from Ormia Lake (Iran) as food for sturgeon. Artemia research and its application, Ecology, Culturing, Use in aquaculture Wetteren: Universa PressSorgeloos P, Bengston DA, Decleir W, Jaspers E 1987, 3:467-468.

Baveghar N, Nasrine G, Feridon G: Geochemistry and the source of salt of Urmia Lake. The First Oceanology Conference of Iran 1998, 20-23.

Eimanifar A, Rezvani S, Carapetian J: Application of RFLP analysis to identify cyst populations of Artemia urmiana (Branchiopoda, Anostraca) from Urmia Lake, Iran. Crustaceana 2005, 78(11):1311-1323.

Eimanifar A, Rezvani S, Carapetian J: Genetic differentiation of Artemia urmiana from various ecological populations of Urmia Lake assessed by PCR amplified RFLP analysis. Journal of Experimental Marine Biology and Ecology 2006, 333(2):275-285.

Handbook of Chemistry and Physics, 63 rd edn., R. C. Weast, ed., CRC Press, Boca Raton, FL, 1982/1983.

Jalali B: A report on Urmia Lake. Tehran, Ministry of Energy 1984.

Jellison K, Romero J, Melack JM: The onset of meromixis during restoration on Mono Lake, California: unintended consequences of reducing water diversions. Limnol Oceanogr 1998, 43:706-711.

Kelts K, Shahrabi M: Holocene sedimentalogy of hypersaline Lake Urmia,northwestern Iran. Paleogeography, Paleoclimatology and Paleoecology 1986, 54:105-130.

Komieli Birjandi D: Study of Salt Extraction in Urmia Lake. MSc Thesis University of Amir-Kabir, Faculty of Chemical Engineering, Tehran, Iran 1999.

Masshovets.V. P., Dibrov . I. A., and Krumgalz . B. S. ; Russ. J. Phys. Chem. 39, 912 (1965).

Mitsch WJ, Gosselink JG: Wetlands John Wiley & Sons, Third 2000.

Romero JR, Melack JM: Sensitivity of vertical mixing in a large saline lake to variation intunoff. Limnol Oceanogr 1996, 41:955-965.

Street-Perrott FA, Roberts N: Fluctuation in closed basin lakes as an indicator of past atmospheric circulation patterns. Variation in the Global Water Budget Reidel, DordrechtStreet-Perrott FA, Beran M, Ratcliffe R 1983, 331-345.

Touloie J: Hydrogeochemistry of Urmia Lake. The First Oceanology Conference of Iran 1998, 20-23.

Van Stappen G, Fayazi G, Sorgeloos P: International study on Artemia LXIII: Field study of the Artemia urmiana (Günther, 1890) population in Lake Urmiah, Iran. Hydrobiologia 2001, 466:133-143.

Table I: The ionic concentration (in molality units) of the Urmia lake water:

Ion	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}
m	5.39	0.069	0.5	0.014	6.18	0.016	0.224

Table II. Results of ΔH_{mix} Measurement for the Procedure: H_2O + Urmia lake Water (with Stirring) at 25ºC

g_{H_2O} (gr)	G_{total} (gr)	$r_{w_{H_2O}}$	I_m	$-\Delta Q_i$ $kJ.(kg\ ULW)^{-1}$	$-\Delta H_{mix}$ $kJ.(kg\ mix)^{-1}$	$-L_1$ $kJ.(kg\ ULW)^{-1}$
0.0100	1.8454	0.0054	7.2675	0.0354	0.0192	3.5489
0.0499	1.8853	0.0265	7.1136	0.1656	0.0879	3.3187
0.0898	1.9252	0.0467	6.9660	0.2836	0.1473	3.1563
0.1298	1.9652	0.0660	6.8245	0.3850	0.1959	2.9669
0.1697	2.0051	0.0846	6.6886	0.4784	0.2386	2.8191
0.2096	2.0450	0.1025	6.5580	0.5487	0.2683	2.6176
0.2496	2.0850	0.1197	6.4324	0.5844	0.2803	2.3417
0.2895	2.1249	0.1362	6.3115	0.6150	0.2894	2.1243
0.2995	2.1349	0.1403	6.2820	0.6154	0.2883	2.0551
0.3394	2.1748	0.1561	6.1667	0.6219	0.2859	1.8323
0.4193	2.2547	0.1860	5.9483	0.5867	0.2602	1.3993
0.4991	2.3345	0.2138	5.7448	0.4850	0.2078	0.9718
0.5790	2.4144	0.2398	5.5548	0.3780	0.1566	0.6528
0.6289	2.4643	0.2552	5.4423	0.3344	0.1357	0.5318
0.7087	2.5441	0.2786	5.2714	0.2639	0.1037	0.3724
0.7886	2.6240	0.3005	5.1110	0.2236	0.0852	0.2835
0.8685	2.7039	0.3212	4.9600	0.2028	0.0750	0.2335
0.9184	2.7538	0.3335	4.8701	0.1784	0.0648	0.1943
0.9982	2.8336	0.3523	4.7329	0.1622	0.0572	0.1625
1.0781	2.9135	0.3700	4.6032	0.1502	0.0515	0.1393
1.2079	3.0433	0.3969	4.4069	0.1224	0.0402	0.1013
1.2877	3.1231	0.4123	4.2942	0.1148	0.0367	0.0891
1.3676	3.2030	0.4270	4.1871	0.1081	0.0337	0.0790
1.4474	3.2828	0.4409	4.0853	0.1021	0.0311	0.0705
1.4973	3.3327	0.4493	4.0241	0.0888	0.0266	0.0593
1.5772	3.4126	0.4622	3.9299	0.0843	0.0247	0.0534
1.6571	3.4925	0.4745	3.8401	0.0802	0.0230	0.0484

In the table II : $g_{H_2O} = 1.8354 \quad (gr)$

Table III. Results of ΔH_{mix} Measurement for the Procedure:

Urmia lake Water + H_2O (with Stirring) at 25ºC

g_{ULW} (gr)	G_{total} (gr)	$r_{W_{ULW}}$	I_m	$-\Delta Q_i$ $kJ.(kg\ H_2O)^{-1}$	$-\Delta H_{mix}$ $kJ.(kg\ mix)^{-1}$	$-L_2$ $kJ.(kg\ H_2O)^{-1}$
0.0122	1.5096	0.0081	0.0592	0.0115	0.0076	0.9376
0.0612	1.5585	0.0393	0.2868	0.0455	0.0292	0.7440
0.1101	1.6075	0.0685	0.5006	0.0709	0.0441	0.6439
0.1591	1.6564	0.0960	0.7017	0.0936	0.0565	0.5882
0.2080	1.7054	0.1220	0.8913	0.1138	0.0668	0.5472
0.2570	1.7543	0.1465	1.0703	0.1337	0.0762	0.5204
0.3059	1.8032	0.1696	1.2395	0.1546	0.0857	0.5054
0.3548	1.8522	0.1916	1.3999	0.1727	0.0932	0.4867
0.4160	1.9134	0.2174	1.5888	0.1961	0.1025	0.4713
0.4650	1.9623	0.2369	1.7314	0.2103	0.1072	0.4523
0.5139	2.0113	0.2555	1.8671	0.2222	0.1105	0.4324
0.5629	2.0602	0.2732	1.9963	0.2356	0.1144	0.4186
0.6118	2.1091	0.2901	2.1195	0.2498	0.1184	0.4083
0.6607	2.1581	0.3062	2.2372	0.2639	0.1223	0.3993
0.7219	2.2193	0.3253	2.3770	0.2707	0.1220	0.3750
0.8198	2.3172	0.3538	2.5852	0.2791	0.1204	0.3404
0.9177	2.4150	0.3800	2.7766	0.2812	0.1164	0.3064
1.0156	2.5129	0.4041	2.9531	0.2759	0.1098	0.2717
1.0768	2.5741	0.4183	3.0566	0.2698	0.1048	0.2506
1.1747	2.6720	0.4396	3.2123	0.2637	0.0987	0.2245
1.2725	2.7699	0.4594	3.3570	0.2534	0.0915	0.1991
1.3704	2.8678	0.4779	3.4918	0.2410	0.0840	0.1759
1.4316	2.9290	0.4888	3.5715	0.2328	0.0795	0.1626
1.5295	3.0268	0.5053	3.6923	0.2216	0.0732	0.1449
1.6274	3.1247	0.5208	3.8055	0.2116	0.0677	0.1300
1.7742	3.2716	0.5423	3.9627	0.1976	0.0604	0.1114

In the table III: $g_{ULW} = 1.497345 \quad (gr)$

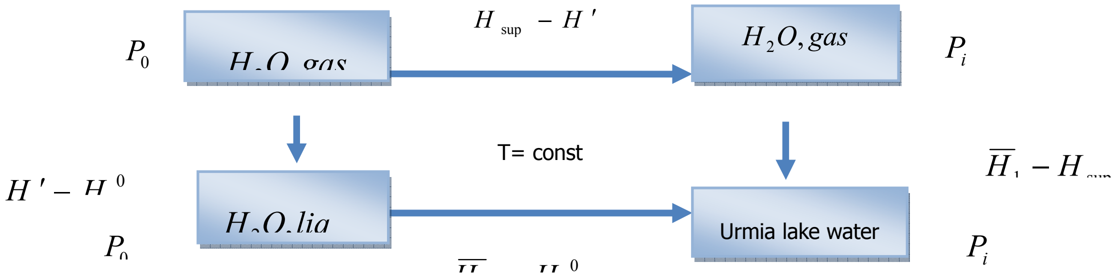

Fig. 1. Isothermal cycle of the dilution of Urmia lake water.

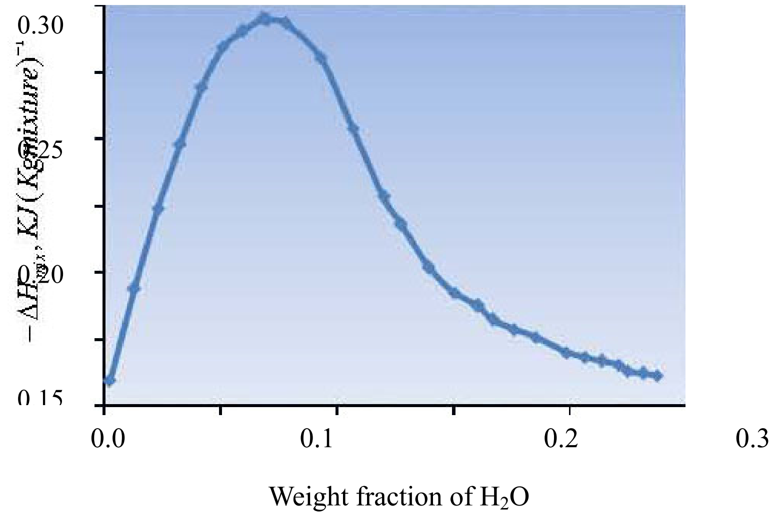

Fig. 2. Heat of mixing of Urmia lake water with fresh water as a function of weight

fraction of fresh water in the formed mixture at $25^\circ C$.

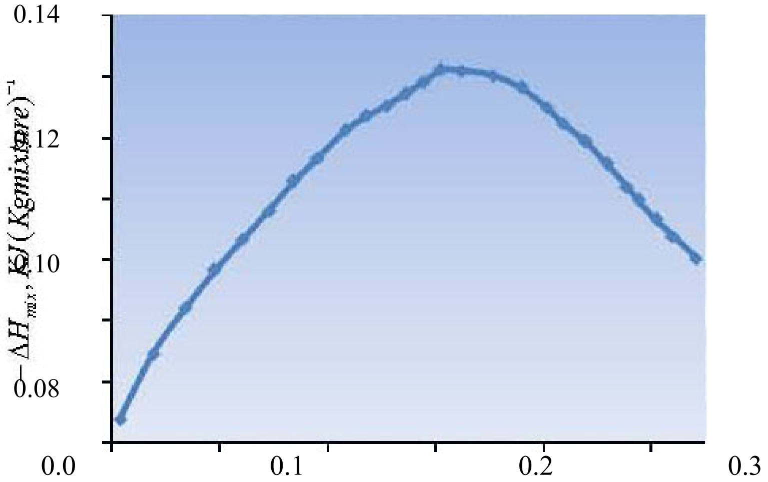

Fig. 3. Heat of mixing of fresh water with Urmia lake water as a function of weight

Weight fraction of ULW

fraction of Urmia lake in the formed mixture at $25^\circ C$.

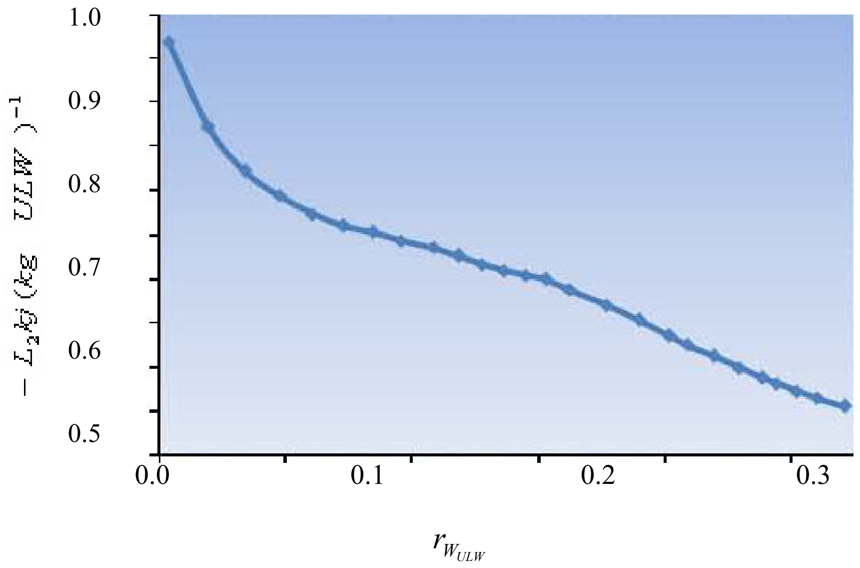

Fig.4. Heat of dilution of Urmia lake water in water at 25ºC as a function of the weight fraction of Urmia lake water in the formed mixtures

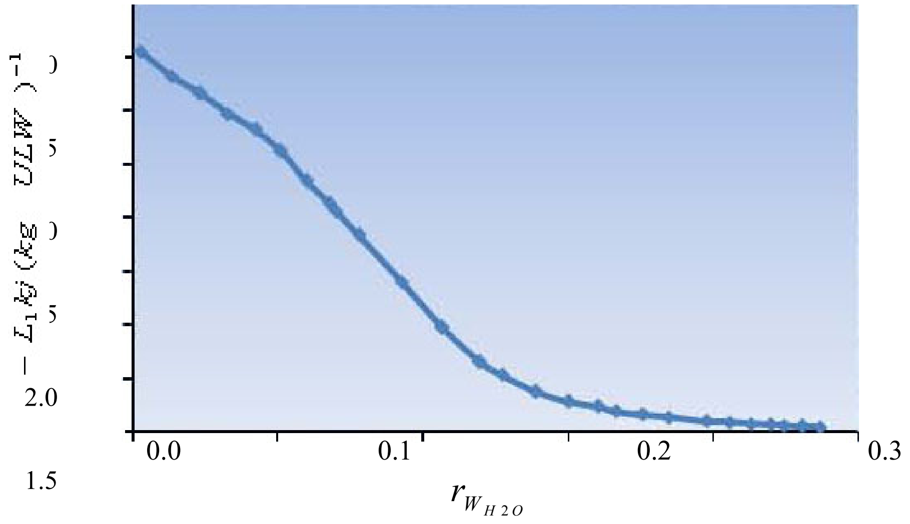

Fig.5. Heat of dilution of water in Urmia lake water at 25ºC as a function of the weight fraction of water in the formed mixtures.

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