**A Reliable & Novel approach based on Thermodynamic Property
estimation of Low to High Salinities Aqueous Sodium Chloride
Solutions for Water-Energy Nexus (WEN) Applications**

Lubna Muzamil Rehman^a, Ranjan Dey^b, Zhiping Lai^c, Asim K. Ghosh^d, Anirban Roy^{a*}

^aDepartment of Chemical Engineering, Birla Institute of Technology and Science-Pilani, K.K Birla Goa Campus, Goa, 403726, India

^bDepartment of Chemistry, Birla Institute of Technology and Science-Pilani, K.K Goa Birla Campus, Goa, 403726, India

^cAdvanced Membranes and Porous Materials Centre, Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwwal, 23955-6900, K.S.A

^dMembrane Development Section, Chemical Engineering Group, Bhabha Atomic Research Centre, Government of India, Trombay, Mumbai, Maharashtra, 400094, India

*Corresponding Author

Email: anirbanr@goa.bits-pilani.ac.in,

Ph No. 00919830265292

Abstract

There is a significant need for reliable and accurate thermodynamic property data of hypersaline solutions to understand the minimum heat and work of separation required and is quite useful for large scale desalination and water – energy nexus (WEN) applications. WEN related technological developments are posed to dominate the scientific pursuits in the coming decade. In this regard, an understanding on the thermo-acoustical parameters of hypersaline NaCl-water systems has been carried out in this study which may lead to a better understanding of WEN. An analysis of thermodynamic properties such as free volume, intermolecular free length, isothermal compressibility, isobaric expansibility, relaxation time, and internal pressures using ultrasonic velocity, has assisted us in understanding the various interactions occurring in hypersaline solutions (up to 100 g/kg). A *new correlation* for internal, osmotic and vapour pressure determination has been proposed in this work. The evaluation of relaxation time showed a minimum value around the concentration range of 25-40 g/kg, which could explain the observed seawater salt concentrations at ambient temperatures. A linear variation was observed between osmotic pressure and internal pressure, which shed light on their interdependency. A detailed analysis on the energetics of hypersaline NaCl-water solutions has also been done to emphasize the fact that one must work on the extraction of osmotic power from hypersaline solutions. This work presents a comprehensive framework derived from an understanding of thermo-acoustical parameters of hypersaline solutions, their critical analysis and a look into its application in Osmotic Power Generation technologies.

Keywords: Hypersaline solutions, ultrasonic velocity, thermo-acoustic properties, Internal Pressure, Water Energy Nexus (WEN).

Nomenclature:

a,b,d,f	Equation constants
b_f	Packing Factor
B/A	Non-linearity parameter
c	Concentration (g/kg)
C.E.D	Cohesive Energy Density (MPa)
d_m	Molecular Diameter (m)
g	Gibbs Free Energy (kJ/kg)
ΔH_{vap}	Heat of Vaporisation (kJ/kg)
k	Constant with value: 4.29×10^9
K	Jacobson's constant
L_f	Intermolecular free length (m)
$\dot{m}$	Mass flow rate of component (kg/s)
M_{eff}	Effective molecular weight (g/mol)
n	C.E.D factor
N	Avagadro Number
P^*	Characteristic Pressure (Pa)
Q_{least}	Least Heat of separation (kJ/kg)
R	Universal Gas Constant (J/mol.K)
T	Absolute Temperature (K)
u	Ultrasonic velocity (m/s)
$\bar{V}$	Reduced Volume (m ³ /mol)
V	Molar volume (m ³ /mol)
V_f	Free volume (m ³ /mol)
W_{least}	Least Work of separation (kJ/kg)
Z	Acoustic Impedance (Pa.s/m ³)
α	Isobaric expansibility (K ⁻¹)
β	Isothermal compressibility (Pa ⁻¹)
β_s	Isentropic compressibility (Pa ⁻¹)
π	Pressure (MPa)
η	Viscosity of the solution (kg/m.s)
ρ	Density of the solution (kg/m ³)
τ	Relaxation Time (s)
$\pi_{i,0}, \pi_{O,0}, \pi_{V,0}$	Equation constants
Subscripts	
p	Product stream
c	Concentrate stream
f	Feed stream
0	Reference state
i	Internal Pressure
O	Osmotic Pressure
V	Vapour Pressure

1. Introduction

It is well reported and agreed upon that the current “state-of-the-art” RO process has helped us reach the thermodynamic limits of desalinating seawater¹. However, there are other challenges which lie ahead of us such as the recovery of RO being at about 40-50%, leaving behind a hypersaline brine, the handling of produced water² and purification of water from hydrofracking operations which has six times the salt concentration as seawater. Treating such streams becomes incredibly challenging because of high osmotic pressures. Also, the irreversibility existing in process design puts a huge energy penalty on the separation processes^{3,4}.

Therefore, understanding salt solutions becomes extremely important in the context of a techno-economic analysis, which has to be carried out beforehand to treat such streams⁵. In this regard, the current study has been undertaken to develop a concrete understanding of such systems. While carrying out this study, the authors understood that there existed a significant gap in literature when it came to NaCl-water systems. It has been reported, albeit sparsely, about a relation between the osmotic pressure and internal pressure of solutions and that osmotic pressure is due to an interaction of the solute and solvent molecules and that internal pressure is a property of the solvent^{6,7}. The estimation of internal pressure of NaCl-Water systems is also challenging as the reported equations for the same are either not applicable to this system or are inconsistent⁸.

The authors resorted to analyse the above problems using a simple ultrasonic interferometric technique. The current work reports, to the best of the author's understanding, for the first time, a direct relationship between internal and osmotic pressures for this system at NaCl concentrations ranging from 0 to 100 g/kg. It is a new relationship between ultrasonic velocity and internal pressure which avoids ambiguity with the existing correlations. Similarly, a correlation for the determination of vapour pressure from ultrasonic data has been proposed for an easy determination of vapour pressure values. A temperature range of 300.15 K to 315.15 K was chosen for the analysis as it covers the ambient temperature range which is prevalent in most tropical countries, while keeping in mind the temperature of feed waters observed in a majority of desalination plants and salinity gradient energy recovery processes across the globe⁹. Studies based on temperatures lying beyond this range are not in the scope of this work as the authors have focused on understanding the various interactions in aqueous sodium chloride solutions for

practical applications which usually deal with feed waters at these temperatures. Also, with a minimal error, values upto 298K at the minimum and 318.15K at the maximum may be obtained by extrapolation as all the property trends have been obtained from highly linear plots. Insights have been drawn on NaCl-water systems from dilute to hypersaline range of concentrations. This was done to analyse the effect of salinity in different feed solutions such as brackish water (0.5 to 30g/kg), seawater (average salinity 35g/kg) and hypersaline water (>35g/kg upto 100g/kg)¹⁰ which would ultimately determine the technology and economics of the process adopted¹¹.

The choice of a suitable desalination process depends upon the salinity of the feed water as well as the minimum amount of heat and work required for the separation of salt from water^{12,13}. In conjunction to this, the values of both vapour pressure and osmotic pressure assist in choosing between a hydrostatic pressure driven separation (such as reverse osmosis) and a thermal separation process (such as membrane distillation)¹². This study also aims at providing an understanding of the best possible choice of a desalination process, which can be made based upon the minimum heat and workload required for a particular salinity of feed water. The authors also emphasize the importance of a water-energy nexus based on the studies carried out¹⁴.

2. Materials and Methods

2.1 Chemicals

Sodium Chloride (Sigma-Aldrich: 99.5%, Germany) was used for preparing salt solutions using Millipore grade water (Arium Advanced, Sartorius, Germany). The solutions were made on parts per thousand (g/kg) basis using a weighing balance of precision $\pm 0.0001g$ (Advanced Performance UniBloc Balance, Shimadzu Analytical Pvt.Ltd, India) and were tested on the same day as they were prepared.

2.2 Density and Viscosity Measurements

Density of the solutions was measured using a pycnometer at different temperatures. Three consecutive readings were taken and the error did not exceed $\pm 0.03\%$. Viscosity measurements were made using an Ubbelholde Viscometer and the readings were compared with literature¹⁵. Three consecutive readings were taken and the error did not exceed $\pm 0.2\%$.

2.3 Determination of Ultrasonic Velocity

Ultrasonic velocity is a characteristic property of a solution¹⁶. It was determined using a multi-frequency Ultrasonic Interferometer (Mittal Enterprises, Delhi, India) at a frequency of 2 MHz at three different temperatures: 300.15 K, 308.15K and 315.15K. Constant temperatures with an error of $\pm 0.01^\circ\text{C}$ were maintained by using a constant supply of water to the Interferometer sample cell (capacity: 7ml) from a water bath (Mittal Enterprises, New Delhi, India)¹⁵. Three readings for each concentration and temperature were taken and the ultrasonic velocity did not deviate more than $\pm 0.2\%$.

2.4 Determination of Thermo-acoustical parameters

The ultrasonic velocity data along with density and viscosity determined at different temperatures, can be used to find the following relations¹⁵ which are characteristic properties of the system:

- (a) Relaxation time (τ) (s):** It is defined as the time required for the compressibility of a solution to reach $1/e$ (about 37%) of its equilibrium value when a constant acoustic pressure is applied upon it¹⁷. It is the least amount of time required for a disturbed system to re-gain stability and is given by the following relation:

$$\tau = \frac{4}{3} \beta_s \eta \quad (1)$$

where, β_s is the isentropic compressibility of the solution and is the reciprocal of the product of the density and square of the ultrasonic velocity ($1/(\rho u^2)$) and η is the viscosity of the solution at a constant temperature.

- (b) Free volume (V_f) (m^3/mol):** It is defined as the free space existing between molecules in a liquid and is related to the degree of molecular interaction and cohesion occurring in the solution^{18,19}. It is obtained using the following equation:

$$V_f = \left[\frac{M_{eff} \times u}{k \times \eta} \right]^{1.5} \quad (2)$$

where, M_{eff} is the effective molecular weight of the solution and k is a constant with the value 4.29×10^9 .

- (c) Acoustic impedance (Z) ($\text{kg}/\text{m}^2\text{s}$):** It is defined as the measure of the obstruction offered for acoustic flow in a solution which results from an applied acoustic

pressure, due to the passage of a sonic wave¹⁸. It is obtained using the following equation:

$$Z = \rho \times u \quad (3)$$

(d) Intermolecular free length (L_f) (m): It is defined as the minimum distance present between two molecules or the distance travelled by a sonic wave between two nearby molecules. It gives an indication of the degree of packing existing in the solution¹⁵. It is obtained using the following equation²⁰:

$$L_f = K \times \beta_s^{0.5} \quad (4)$$

where, K (Jacobson's Temperature dependant constant: $(93.875 + 0.375 \times T) \times 10^{-8}$, T being the absolute temperature (K).

(e) Non-linearity parameter (B/A): The intensity or amplitude of sound waves coming out of a transducer are finite for all practical applications. The measurements of ultrasonic propagation constants become unreliable when sound waves of finite amplitude and high intensities propagate in fluids since non-linear effects like acoustic streaming and distortion of the waveform occur due to greater attenuation of high frequency constants compared to low frequency ones²¹. The fundamental approach to deriving governing equations for non-linear ultrasonics is based on the classical fluid mechanics approach for solving the mass conservation, momentum and energy balance equations. Bjørnø^{21,22} used the perturbation theory approach to solve a set of 6 equations and to derive the 1st and 2nd order ultrasonic equations. It can be observed that B/A is governed by the derivative of sound velocity with respect to temperature and pressure, thus B/A is called the second order non-linearity parameter. It has been reported that the molecular structure and intermolecular / interatomic potentials has a close relationship with B/A ²³. Since then, a lot of work has presented the significance of B/A .

The property has multifarious applications including determining the efficiency of devices that are based on acoustic nonlinear mixing. There are several other technical applications which include harmonic imaging in biological media and parametric sonar imaging²³⁻²⁶. One of the empirical relations used to find this parameter was given by Beyer²⁷ and is as follows:

$$\frac{B}{A} = -0.5 + (1.2 \times 10^4)/u \quad (5)$$

(f) Internal Pressure (π_i) (MPa): It is defined as the change in internal energy with volume at constant temperature. It is an important parameter which describes the degree of constriction and pressurization occurring in a solvent due to the addition of a solute and must not be confused with external pressure. It is a thermodynamic parameter derived from fundamental property relations. The internal pressure of salt-solutions was determined using different relations reported in literature and has been compared to empirical correlations^{8,28}:

(i) Flory's relation²⁹: $\pi_i = \frac{\alpha T}{\beta}$ where, $\alpha = \frac{3(\bar{V}^{\frac{1}{3}}-1)}{[1-3(\bar{V}^{\frac{1}{3}}-1)]T}$ and $\beta = \frac{\alpha \bar{V} T}{P^*}$ (6)

where, α is the isobaric expansibility, β is isothermal compressibility, $\bar{V}$ is the reduced volume and P^* is the characteristic pressure of the solution.

(ii) Buehler–Hirschfelder–Curtiss equation of state relation for internal pressure³⁰:

$$\pi_i = \frac{2^{1/6} RT}{2^{1/6} V - d_m N^{1/3} V^{2/3}} \quad (7)$$

where, V is molar volume, d_m is molecular diameter, N is Avagadro's number, and R is universal gas constant.

(iii) Suryanarayana's relation³¹: $\pi_i = b_f RT \left(\frac{k \times \eta}{u} \right)^{0.5} \frac{\rho^{0.67}}{M_{eff}^{1.17}}$ (8)

where, u is the ultrasonic velocity of the solution b_f is the molecular packing factor and is assumed to be "2" for all liquids, T is the absolute temperature of the solution, ρ and η are the density and viscosity of the solution respectively, M_{eff} is the effective molecular weight of the solution, and k is a constant with a value 4.29×10^9 .

(iv) Empirical correlation: $\pi_i = \frac{\alpha T}{\beta}$ (9)

where, α and β have been obtained from ultrasonic velocity relations. The relations are as described in previous work²⁸.

(g) Cohesive Energy Density (MPa): It is defined as the total measurable cohesion occurring within a solution between molecules of different components, per ml of the solution. It gives the total contribution of chemical and non-chemical interactions, be it dipole–dipole or hydrogen bonds, to the bonding energies of the system. It is obtained by a simple relation as follows³²:

$$C.E.D = \frac{\Delta H_{vap} - RT}{M_{eff} / \rho}$$
 (10)

where, ΔH_{vap} is the heat of vaporisation of the solution.

The C.E.D of water and other polar associated solvents is much greater than their internal pressures. A factor defined as “n” is obtained as per the ratio below:

$$n = (\pi_i / C.E.D)$$
 (11)

The cohesiveness of a solution is defined by the value of this factor “n”. If $n \geq 1.20$, these solutions are characterized as “loose” solutions, such as piperidine and tetramethyl urea, among others. Whereas, solutions with ratios $n \leq 0.8$ are characterized as “tight” solutions such as, water and formamide, among others. Also, the value of $(C.E.D - \pi_i)$, gives a measure of the intermolecular hydrogen bonding energy occurring in the system³². This value is predominant in salt-water solutions due to strong electrostatic interactions.

Table 1 gives a comparison of the quantities experimentally determined and the values reported in literature. It is important to note that the frequency of the ultrasonic wave must be maintained constant while determining the ultrasonic velocities of acoustic waves through different concentration salt solutions and varying temperatures. The variation of frequency of the wave would also affect its wavelength and consequently its velocity. Therefore, ultrasonic velocities of pure water at temperatures in the range of 300.15K to 315.15K have been experimentally observed at a frequency of 2MHz and have been compared with literature values reported at identical frequencies, in Table 1. Also, the densities and viscosities were carefully determined at accurate temperatures which were maintained using a calibrated water-bath and the values have been compared with literature as shown in Table 1.

Table 1: Comparison of experimental Densities, Viscosities, and ultrasonic velocity of water with Literature Data at different temperatures.

Temperature (K)	Density (kg/m ³)			Viscosity x10 ⁴ (kg/m.s)			Ultrasonic Velocity (m/s)		
	Expt.	Lit ³³	%dev.	Expt.	Lit ³³	%dev.	Expt.	Lit ^{33,34}	%dev.
300.15	996.49	996.42	0.01	8.53	8.54	0.1	1503.17	1502.24	0.06
308.15	994.03	993.94	0.01	7.23	7.25	0.27	1521.10	1519.00	0.13
315.15	991.07	991.38	0.03	6.31	6.31	0	1533.10	1531.00	0.13

3. Results and Discussion

3.1 Thermo-acoustical Properties

The values of density, viscosity and ultrasonic velocity of aqueous Sodium Chloride solutions at different temperatures are as shown in Table 2. A detailed tabulation of data in Table 2 is available in the supplementary information.

Table 2: Tabulation of NaCl-solution properties at different temperatures:

Temperature (K)	Concentration (g/kg)	Viscosity $\times 10^4$ (kg/m.s)	Density (kg/m ³)	Ultrasonic Velocity (m/s)
300.15	0	8.53	996.498	1503.172
	25	8.972	1014.917	1532.551
	50	9.505	1033.925	1562.344
	75	10.128	1053.411	1586.621
	100	10.844	1072.221	1610.483
308.15	0	7.236	994.031	1521.103
	25	7.610	1018.774	1545.517
	50	8.069	1035.150	1575.172
	75	8.600	1051.083	1591.862
	100	9.209	1069.095	1618.069
315.15	0	6.310	991.073	1533.103
	25	6.673	1010.475	1557.241
	50	7.082	1026.35	1583.448
	75	7.550	1043.269	1597.931
	100	8.082	1063.297	1622.897

The degree of uncertainties in viscosity was: **0.2%**, in density was: **0.03%**, and ultrasonic velocity was: **0.2%**.

As can be seen in Table 2, the values of density and viscosity are increasing with the increase in concentration of sodium chloride in the solution (at constant temperature). Also, a gradual increase in ultrasonic velocity with concentration as well as temperature can be observed. While a decrease in both viscosity and density can be observed for the same concentration solution, with a temperature increase.

Fig 1: Plot of Ultrasonic Velocity and Concentration with varying Temperatures

From Fig 1, a linear relation can be observed between ultrasonic velocity and concentration at all temperatures. It is clear that this property increases steadily with increasing temperature³⁵. The aqueous solutions of NaCl contain clusters of salt ions and water molecules-influenced by hydrogen bonding and ion-dipole interactions, which increase with an increase in salt concentration³⁶. This cluster growth at a constant temperature facilitates higher ultrasonic velocities of the acoustic wave, which can be observed in Fig.1. As the temperature continues to increase, the size of each cluster reduces even though the number of clusters increases. Bharmori et.al³⁶, observed that with a significant increase in both concentration and temperature of aqueous NaCl solutions, the observed size reduction of these clusters is almost insignificant. This means that NaCl clusters were temperature stable. In Fig.1, the reduction in slope of the graph shows that the ultrasonic velocity begins to vary less with temperature increase than with a solute concentration increase. The effect of concentration of NaCl in the solution is more pronounced than the temperature for an ultrasonic wave as observed. This explains a very important effect of interaction between the acoustic wave and the salt cluster growth.

Fig 2: Plots of Free length and Acoustic Impedance at different temperatures

Fig 2(a) shows that the intermolecular free length (L_f) is gradually reducing with increasing concentrations of salt in water. This shows that there is a strong attraction between ions of the electrolyte and the water molecules. This would also explain the important phenomenon of volume electrostriction existent in electrolyte solutions. Another important observation is that the solute-solute interactions are not as significant as solute-solvent interactions and this figures in the reduction in free length (L_f) parameter. Also, an increase in the free length value with temperature is observed. This is because L_f is a temperature dependant parameter (based on Jacobson's constant) and increases with an increase in temperature. Isentropic compressibility of NaCl-water solutions is very low and shows very minute changes with temperature, which can be attributed to the strong electrostrictive effect produced by the Na^+ ions in the solution³⁶. Thus, free length (L_f) which is a function of the compressibility, tends to vary less significantly with concentration at higher temperatures than it does at lower temperatures.

On the other hand, there is a gradual increase in the trend of Acoustic Impedance (Z) as shown in Fig 2 (b). The acoustic impedance of an aqueous NaCl solution is a function of the salt concentration and temperature. Ultrasonic velocity and temperature increase linearly with each other, and acoustic impedance varies directly with ultrasonic velocity as observed in Fig.2 (b) and obtained from Eq 3. The highest ultrasonic velocities were observed at a concentration of 100g/kg for all the temperatures (300.15 K, 308.15 K and 315.15K). At higher temperatures, the degree of solvation of ions in water increases, and the acoustic impedance begins to reduce with respect to temperature³⁷. This phenomenon

is explained from the “overlap” of curves observed in Fig 2 (b). The inherent resistance to the passage of the ultrasonic wave reduces as more ions are surrounded by water molecules to form clusters resulting in a reduced slope at 308.15 K and 315.15 K as compared to that observed at 300.15 K³⁸.

Fig 3: Plots of Free Volume and Relaxation Time at different temperatures

The graph of free volume (Fig 3 (a)) shows a sweeping decline with an increase in concentration of the salt in the solution and a subsequent increase with temperature. The free volume (V_f) of a solution is the net volume left unoccupied between neighbouring molecules in the solution¹⁹. This property reiterates our understanding that the changes in the solvent structure result in the property changes of electrolyte solutions rather than the effect of the size of the ions in the solvent³⁹. This can be explained by observing Fig 3 (a) in which the V_f of the solution begins to reduce with an increase in salt concentration. As the solvation of salt crystals in the solution increases with temperature, the liberated ions begin to attract water molecules towards themselves, thereby increasing the unoccupied space or volume initially present between the molecules. An interesting observation is the steady increase in the observed V_f values with temperature which occurs by almost the same amount for a particular concentration. For instance, at 100 g/kg the free volume (V_f) increases by a factor of about $0.51 \times 10^{-8} \text{ m}^3/\text{mol}$ from its value at 300.15 K to its value at 308.15K and by a similar factor from its value at 308.15K to its value at 315.15K. This trend is replicated in other concentrations as well which may be due to the linear

dependency of the parameters that V_f is a function of (u and η) with temperature and concentration. At salt concentrations upto 25 g/kg at 300.15 K, the amount of ions in the solvent is not too significant to cause a strong electrostriction and reduce the entropy of the solution⁴⁰. As the increase in concentration of salts in the solution occurs, a subsequent strong electrostriction effect and gradual decrease in V_f is observed. The solvated ions at higher temperatures disperse into the solution and occupy spaces existing between solvent molecules resulting in an apparent increase in V_f . It can also be explained by the existence of unbonded and free molecules at higher temperatures, resulting in a higher value of V_f ¹⁹.

Upon perusal of Fig 3 (b), it is observed that relaxation time (τ) which is the least amount of time taken for the solution to regain about 36.79% of its equilibrium state upon being disturbed by the passage of an ultrasonic wave through the solution, and thereby imparts an acoustic pressure on the solution, increases with concentration after crossing a minima and also reduces with temperature. As can be seen in the graph, a clear dip in these values occurs at around 25-45 g/kg concentration of NaCl solution, after which it gradually increases. It can be clearly observed in an enlarged image of the trend given in Fig 1 in the supplementary information. This observation is more significant at lower temperatures than at higher temperatures. The kinetic energy of molecules of water increases with an increase in temperature and the “dip” or reduction in slope of the curves observed at lower temperatures disappears at higher temperatures and is replaced by an almost linearly increasing trend in this concentration range. Nevertheless, at ambient conditions (300.15 K and 308.15 K and lower temperatures beyond the scope of this work, a similar trend with lower relaxation times (τ) in the 25-40 g/kg range can be observed). Therefore, it may be said that the most stable concentration for seawater is observed at 25-40 g/kg. This would probably answer a very crucial question of why the seas and oceans around the world attain an average concentration of 35 g/kg and exist in salinities lying around this average value⁴¹. A reduction of the relaxation time (τ) with a subsequent increase in temperature is observed. This is attributed to the reduction in disturbances and distortion of the ultrasonic wave²². As the solution components already have an increased internal energy due to the temperature increase, it takes lesser time to reach this excited state after an acoustic disturbance in the medium.

Fig 4: Plots of B/A non-linearity parameter at different temperatures and concentrations

The non-linearity parameter shows a gradual decrease with concentration (Fig 4) as well as temperature. The two major contributing factors to the non-linearity of a pure liquid or a mixture is the dissipation observed when the ultrasonic wave propagates through the medium at a certain frequency and distance from the ultrasonic source, and the non-linearity which leads to the formation of higher harmonics at higher intensities. These two effects counteract and contribute to the “distortion” of the wave which results in higher B/A values or non-linearity of the medium. Dissipation increases with viscosity and heat conductivities while the non-linearity effect mainly depends on the intensity of the wave and the distance covered by the ultrasonic wave. A gradual reduction in B/A value with concentration at a constant temperature can be attributed to a reduction in distortion of the wave. A simple explanation of this is that the travelling sonic wave is not sufficiently distorted at higher concentrations due to the formation of ion-molecule clusters which reduce the effects of intensity on the wave and thereby do not result in the generation of higher order harmonics at the cost of dissipation of energy from the fundamental wave. At higher temperatures, the value of B/A reduces slightly which can be due to the increase in free volume (V_f) and reduction in relaxation time (τ) of the system which reduces the effects of distortion. It can also be due to the reduction in viscosity and density of the solution which are contributing parameters to the thermodynamic B/A factor. However, at higher concentrations ($>70\text{g/kg}$), this variation with temperature becomes less significant²¹. It is also important to note that the non-linearity in a medium arises due to the effect of an acoustic disturbance and cannot be compared to the ideality of the system as non-linearity may exist in both ideal and non-ideal systems.

3.2 Internal Pressure

Table 3: Tabulation of the published equations for determination of internal pressures of various systems.

Equation Proposed by	Equations Proposed for determination of Internal Pressure	Observations
Flory	<i>Eq (6)</i>	Stark disagreement with experimentally determined values at higher concentrations of salt solution
Buehler–Hirschfelder–Curtiss equation of state	<i>Eq (7)</i>	Obtained from thermodynamic EOS for Rigid sphere liquid molecules and may not be applicable to salt-water systems
Suryanarayana	<i>Eq (8)</i>	Gives very high values of Internal Pressure- of the order of 2600 MPa

Fig 5: Comparison of internal pressure values obtained by employing different correlations: Buehler–Hirschfelder–Curtiss EOS (B-H-C curve), Flory's relation (Flory's

curve) and Empirical relation based on ultrasonic velocity (Empirical curve) at a constant temperature of 300.15 K.

Table 3 discusses the various issues arising from the usage of the respective equations for NaCl-water solutions. From Fig 5, a clear deviation can be observed between the π_i values determined using the empirical correlation and by using the other two relations. Also, it is important to note here that the π_i values determined using Suryanarayana's correlation is of very high magnitudes $>2600\text{MPa}$, and therefore could not be shown in Fig 5. This must be due to the assumption that a packing factor of "2" is applicable to all pure non-polar solvents. The effect of packing in an electrolyte solution is rather complex with ion-ion repulsion and ion-dipole attractive forces contributing to the interactions. Assuming cubic packing factor is an approximation that did not yield accurate results for this system. Also, it may be applicable more to non-polar solvents and pure liquid mixtures than other complex solutions. Although it is a very simple approach based on dimensional analysis for the determination of internal pressure, it gives exorbitantly high values for this system and thus could not be used for further calculations.

The plot for Flory's relation shows a decrease and a subsequent increase in values which goes against the trend reported for internal pressures of electrolyte solutions⁶. This is mainly because the statistical thermodynamics relation developed by Flory is applicable to non-polar liquids and their mixtures containing molecules which differ in size and shape. The determination of internal pressure involves the correct correlation of isothermal compressibility of the aqueous electrolyte solutions which is again dependant on the internal energy and free volume of the solution. Flory's relation assumes a "hard sphere repulsive potential" which may be the reason why it is not giving acceptable results for an aqueous salt solution which is a model containing cations and anions surrounded by oriented water molecules.

Similarly, the Beuhler EOS did not vary significantly with concentration of salt and this may be because the Beuhler EOS was applicable to rigid volume sphere solutions, and thus may not be applicable to this ion-water molecule system³⁰. An extensive study on the packing of molecules of liquids at low and high densities and its effects on orientation and arrangement of molecules of liquids around each other has been done by Buehler et al. which is again based on the "free volume" concept. As can be observed from Eq 7, the main parameters considered are the molar volume and temperature of the solution. At

constant temperature, the only parameter that would vary would be the molar volume of the solution with an increase in salt concentration. Thus, the denominator on the right hand side of Eq 7 is the factor which affects the value of the internal pressure. Since molar volume of an aqueous NaCl solution decreases with an increase in amount of NaCl crystals in solution, the internal pressure must increase. However, this change is not effectively captured in the equation and thus fails to give accurate results. Also, the diameter of the solvent molecule is considered in the calculation which may be incorrect as the internal pressure has more to do with the free volume existing in the solution rather than the solvent molecule itself-although it does influence the free volume determination.

Fig 6: Direct relationship between internal pressure and ultrasonic velocity

The plots of internal pressure (determined from Eq (9)) with concentration depict a linear relation between the two parameters as is shown in Fig 6(a). The error of measurement is $<0.05\%$, hence error bars have not been shown in Fig 6. The internal pressure of the solution increases with temperature. However, this temperature dependency of the property reduces at higher temperatures as the slope of the curves is observed to be gradually reducing. A highly linear trend is observed in the relation between internal pressure and ultrasonic velocity (Fig 6 (b)) which makes the determination of internal pressure from ultrasonic velocity data all the more accurate and easy. Thus, deviations from experimental data observed in other prescribed equations were corrected for by furnishing a new correlation for the determination of internal pressure of NaCl-water solutions in this temperature range (Eq 12 in Table. 4). The same has been shown as a curve fit in Fig 7.

Fig 7: Surface fit for internal pressure as a function of concentration and temperature

3.3 Osmotic Pressure

Osmotic pressure data is very important in the field of desalination. Operations and processes such as reverse osmosis and forward osmosis run on the concept of osmotic pressure difference^{42,43}. This study has attempted to bridge the gap between the understanding of internal and osmotic pressure of a solution by defining them as related parameters. This has been established by experimentally analysing the interdependence of these properties. The internal pressure of the solution is a characteristic property of the solvent in a solution and is related to the osmotic pressure which is a colligative property and depends on the amount of solute or salt added to the solution⁷.

Fig 8: Direct relationship between internal pressure and osmotic pressure

Fig 9: Relationship between internal pressure and osmotic pressure with respect to concentration

As can be seen in Fig 8, osmotic pressure varies directly with internal pressure. Both these properties show a dependence on amount of solute added to the solvent. However, the slope of the curves in Fig 8 are increasing as the temperature increases which shows that the osmotic pressure is more sensitive to a temperature change than is internal pressure. Whereas in Fig 9, it can be observed that the change in osmotic pressure with temperature becomes more significant at higher concentrations. The inset graph explains the increase in osmotic pressure at higher concentrations and temperatures. The highly

linear trend of osmotic pressure with ultrasonic velocity led to the development of a simple correlation (Eq 13) for the quick determination of osmotic pressure from ultrasonic velocity data (Fig 10 (a) and (b) and Table 4).

Fig 10: Surface fit for osmotic pressure as a function of ultrasonic velocity and concentration

3.4 Vapour Pressure

The significance of vapour pressure as a colligative property is well know. It has a significant role to play in thermal desalination processes. This property can be used to explain the nature of transport of water molecules across hydrophobic membranes and is the driving force in membrane distillation⁴⁴. The observed trend for the variation of vapour pressure of NaCl-water solutions with ultrasonic velocity was fairly linear and thus a simple correlation (Eq 14) for the determination of this property from acoustical data has been obtained as shown in Fig 11 (a) and (b). As expected, a gradual increase of vapour pressure with temperature and a gradual decrease in vapour pressure with concentration is observed. The simple correlation is provided in Table 4.

(a)

(b)

Fig 11: Surface fit for vapour pressure as a function of ultrasonic velocity and temperature

The properties discussed in sections 3.2, 3.3 and 3.4 have been summarised as correlations in Table 4.

Table 4: Compilation of the proposed correlations for π_i , π_o , and π_v :

Thermodynamic property	Equations (c, u and T are in g/kg, m/s and K respectively)
Internal pressure π_i (MPa)	$\pi_i = \pi_{i,0} + a * c + b * T + d * c^2 + e * T^2 + f * c * T \quad (12)$ <p>where, $\pi_{i,0} = -8952.14$, $a = 8.61$, $b = 52.93$, $d = -5.4E-04$, $e = -0.075$, $f = -0.025$,</p>
Osmotic pressure π_o (MPa)	$\pi_o = \pi_{o,0} + a * u + b * c + d * u^2 + e * c^2 + f * u * c \quad (13)$ <p>where, $\pi_{o,0} = -510.486$, $a = 0.674$, $b = -1.058$, $d = -2.226E-4$, $e = -3.087E-4$, $f = 7.415E-4$</p>
Vapour pressure π_v (kPa)	$\pi_v = \pi_{v,0} + a * u + b * T + d * u^2 + e * T^2 + f * u * T \quad (14)$ <p>where, $\pi_{v,0} = 402.1382$, $a = 0.1108$, $b = -3.4322$, $d = -1.6133E-05$, $e = 0.00661$, $f = -2.0889E-04$</p>

3.5 Cohesive Energy Density

Table 5: Tabulation of the results obtained at different temperatures.

Temperature (K)	Concentration (g/kg)	CED (MPa)	(C.E.D - π_i) (MPa)	n
300.15	0	2290.319	2102.712	0.082
	25	2334.958	2116.161	0.094
	50	2380.627	2130.668	0.105
	75	2426.904	2149.425	0.114
	100	2471.598	2167.416	0.123
308.15	0	2261.984	2009.634	0.112
	25	2320.75	2045.868	0.118
	50	2360.169	2059.687	0.127
	75	2398.123	2083.041	0.131
	100	2440.808	2099.384	0.139

315.15	0	2235.5	1943.576	0.131
	25	2281.779	1969.561	0.137
	50	2319.829	1986.752	0.144
	75	2359.9103	2009.949	0.148
	100	2407.009	2033.85	0.155

The degree of uncertainty in cohesive energy density determination was 0.03% and internal pressure determination was less than 0.05%.

Fig 12: Comparison of contribution of hydrogen bonding to C.E.D at different concentrations and temperatures.

The value of cohesive energy density gives the contribution of molecular energy which results in a cohesion of molecules per millilitre of solution. While cohesive energy density and internal pressure are two different quantities, they may be related as has been explained in the previous section. In Table 5, it can be observed that very high values of C.E.D occur due to the contribution of hydrogen bonding. Also, the contribution to cohesion varies significantly with the variation of hydrogen bonding and increases with an increase in concentration of salts in water as the molecular interactions also increase³². The strong electrostriction of ions causes a further increase in C.E.D values at a constant temperature. Fundamental understanding of activity coefficients has led researchers to understand that the basic approximation of ideal gas laws to dilute aqueous sodium chloride solutions in order to explain ideality of the solutions, is incorrect as activity

coefficients of highly concentrated electrolyte solutions are much greater than unity⁴⁵. This question can be answered by understanding the relation between activity coefficients and molar cohesive energy (kJ/mol). Previous work has established this relation which shows that the behaviour of the solvent is due to the variation of the molar cohesive energy of the solution with respect to the molar cohesive energy of the solvent which in turn is dependent upon the internal pressure of the solution^{45,46}. It also states the non-ideality of the solution observed at higher concentrations of salt is due to the increase in molar cohesive energy densities as is observed in Table 5.

The internal pressure of solutions measures the non-chemical contributions to the C.E.D. Therefore, the hydrogen bonding energies can be obtained from $(C.E.D - \pi_i)$ ⁴⁶. In Fig 12, the variation in the degree of hydrogen bonding is explained as a function of temperature and concentration, which is mentioned at the top of every coloured bar in g/kg. It explains the increase in hydrogen bonding energies with an increase in salt concentration which also indicates an increase in molecular interactions and further shows that there is a stronger cohesion of molecules at a constant temperature⁴⁶. Since the values of C.E.D define the energy associated with the breakage of electrostatic attractive forces and internal pressure is associated with the change in internal energy with small changes in volume, the significantly small “n” values are accounted for as a tight or stiff solution performance which occurs even at high concentrations of salt. This phenomenon is observed in solutions which have strong hydrogen-bonding and ion-water interactions present in them³².

However, with an increase in temperature, the $(C.E.D - \pi_i)$ values reduce for a particular concentration of NaCl-water solution as shown in Fig 12. The percentage decrease from 300.15 K to 308.15 K and subsequently 308.15 K to 315.15 K ranges between 3-4% for all concentrations of NaCl upto 100 g/kg. This is due to the increase in molar volume and unbonded molecules resulting from an increase in temperature and excitation of the solution. The “n” factor subsequently increases indicating that the solution is tending towards the “loose” solution category as has been explained in section 2.

4. Implication of π_i , π_o , and π_v measurements: Case study for Water-Energy Nexus

The relationships and understanding developed in the preceding sections have an important implication in water energy nexus problems. The question to be asked at this

juncture is that given a salinity do we recover fresh water from the stream or utilize the salinity gradient to generate power. Desalination technologies have moved beyond conventional reverse osmosis and is venturing into membrane distillation (for high salinity streams). Fabrication of advanced membranes capable of making pressure retarded osmosis (PRO) and reverse electrodialysis (RED) feasible is still being researched. These technologies use salinity gradients to recover energy from mixing streams. Therefore, for a given stream of unknown composition, the discussed framework can be used as a facile technique to evaluate π_i, π_o , and π_v from the inputs of only salinity and ultrasonic velocity and by using this knowledge, a decision can be taken on how to handle the streams.

The energetics of separation are equal to energetics of mixing for a thermodynamically reversible process. The separation of a stream involves two forms of energy, namely work and heat. Although they are treated in a similar manner, they are different from a thermodynamics perspective. The benchmark values of least heat and least work of separation for a stream can be calculated as reported in literature⁴⁷ and is discussed below. A schematic representation of the process is as shown in Fig 13. Hypersaline solution is fed as feed to the desalinating plant which is separated to give a concentrated brine and pure water stream respectively. The driving forces for desalination may be a pressure difference (reverse osmosis) or a temperature difference causing a vapour pressure gradient (membrane distillation (MD), multi-effect distillation (MED)). In Fig 13, RO process would require the feed to be pumped at hydraulic pressures greater than the osmotic pressure of the solution to result in the desalination of water. While for an MD process, the pressurized hypersaline feed is additionally heated to temperature ($T > T_0$, where T_0 is the cold stream temperature) before being passed through the desalinating unit². Therefore, analysing the amount of energy required for both these processes is crucial for making an unerring judgement between desalination and energy production for hypersaline solutions.

Fig 13: Schematic Representation of Desalination Process

The least work of separation is a function of temperature, feed and product salt concentration, and recovery ratio and is plotted for various feed salinities (<60 g/kg) and a 50% recovery ratio at a constant temperature of 300.15 K, in this study. The least work of separation data will be applicable for processes which require a hydraulic pressure to be applied to initiate recovery of fresh water, such as reverse osmosis and electrodialysis. The energies required for 50% recovery of fresh water from feed concentrations upto 60 g/kg were analysed. The least work of separation is calculated from the following relation⁴⁷:

$$\frac{\dot{W}_{least}}{\dot{m}_p} = (g_p - g_c) - \frac{1}{r}(g_f - g_c) \quad (15)$$

where, $\dot{m}_p$ is the mass flow rate of the product stream; and g is the specific gibbs energy⁴⁸.

Fig. 14: Least work of separation at $T_0 = 300.15$ K obtained for two different product stream concentrations; 0 g/kg and 0.5 g/kg

From Fig. 14, least work of separation of feed stream containing different concentrations of salts can be found for a 50% recovery of feed water. Lesser amount of energy is required to obtain a 0.5g/kg concentration product (drinking water) than for a 0g/kg product stream. At lower concentrations (<15g/kg), the same amount of work will have to be supplied by pumps to produce 0.5g/kg and 0g/kg product water.

Similarly, the least heat of separation was obtained for analysing the amount of heat required in thermal desalination processes, such as, multi-effect distillation, membrane distillation and multi-Stage flash, and as shown in Fig.12. The energies required for 50% recovery of fresh water from feed concentrations upto 60g/kg were analysed. The least heat of separation is calculated from the following relation⁴⁷:

$$\frac{\dot{Q}_{least}}{\dot{m}_p} = \left(1 - \frac{T_0}{T}\right)^{-1} \left[(g_p - g_c) - \frac{1}{r} (g_f - g_c) \right] \quad (16)$$

where, T_0 is the reference temperature (300.15K), and T is the temperature of the hot stream (as shown in Fig.13). The analysis was done for low grade heat which is available at temperatures ranging from 313.15K to 353.15K in most thermal desalination plants.

Fig. 15: Least Heat of Separation for 50% recovery and $T_0 = 300.15$ K

From Fig 15, an understanding of the relation between the least heat of separation and the temperature of the hot stream can be obtained. As observed, the least heat of

separation reduces at higher top temperatures. This is in agreement with the Second law of Thermodynamics and Carnot Efficiency. At very high salinity of feed water, more amount of heat is required for separation of water and salts (~40 to 160 kJ/kg depending upon the top temperature). This analysis leads to the understanding that to treat hypersaline solutions of concentrations 60g/kg and above, one must operate at high thermal and pressure gradients to achieve best possible separation and recovery of fresh water. Hence, these streams can instead be used for the extraction of thermal/osmotic gradient energy before being discharged into oceans and seas⁴⁹.

5. Developing a Framework for Water Energy Nexus

Fig: 16 Framework for Desalination-Water Energy Nexus

A clear understanding of the proposed work can be obtained from Fig 16. The previous methodology involved the determination of the salinity and temperature of the feed stream before calculating osmotic and vapour pressures, while the internal pressure of the stream was not determined. In the proposed technique, if given a stream of water of unknown concentration, ultrasonic velocity of the stream can be. This value is a characteristic property of the solution at a constant temperature and concentration of salt

(salinity). Osmotic pressure, internal pressure and vapour pressure can then be determined using the thermodynamic relations proposed in this study. A decision can then be taken as per the cut-offs of the respective values as shown in Fig 16, whether one must opt for desalination based on osmotic pressure difference (reverse osmosis, forward osmosis) or based on a vapour pressure difference due to a thermal gradient existing between the concentrated and draw solution (membrane distillation) or to opt for recovering salinity gradient power (thermo-osmotic energy conversion: TOEC, pressure retarded osmosis: PRO, reverse electro-dialysis: RED) from the water stream.

There have been a lot of reports and more so in recent times on desalination–salination technologies⁵⁰, hybrid thermal desalination technologies⁵¹, low grade heat desalination⁵² as well as solar integrated desalination⁵³. These approaches utilize either vapour pressure or hydraulic pressure as the driving forces for water production in view of the WEN approach. Also, there are reports on salinity gradient power generation^{54–56} as well in recent literature. These emphasize that the two research areas are gaining widespread popularity, and that there is a need to bridge the understanding between the two approaches as well, i.e., “water from power” and “power from water”. Hence the current effort is designed specifically to bridge the gap and develop engineering understanding of WEN for such approaches

6. Conclusion

The thermo-acoustical properties indicate an existing interaction in aqueous sodium chloride solutions, ranging from low to high salinities. It was observed that the relaxation time of the system (from 300.15 K to 315.15 K) decreased upto a certain salinity (25-40 g/kg) and then increased as temperatures increased which was due to the interactions between water molecules and electrolyte ions. Another important observation was that at ambient temperature, there was a decrease in relaxation time in the region of 25- 40g/kg, which might explain the salinity of seawater to be the same as that observed in nature. It was also observed that the free length and free volume increased with increase in temperature which is attributed to an increase in unbonded molecules in the solution.

A facile equation has been proposed for determining internal pressures of NaCl-water systems. Consequently, relationships between osmotic and vapour pressures have also been determined. The authors observe that internal and osmotic pressures, of NaCl-water system, are related in a linear fashion. Also, the variation of osmotic pressure is more significant than internal pressures at higher temperatures.

This study employs thermodynamic equations to understand the minimum heat and work of separation of hypersaline solutions, and therefore, proposes that at higher salinities, it is important to utilise salinity/vapour pressure gradients to generate power—than work against it to produce water. For this, technologies like thermo-osmotic energy conversion, pressure retarded osmosis, reverse electrodialysis, should be explored at a commercial scale. A framework for the sound judgement between desalination and water energy nexus (WEN) applications has also been developed which is made based on two factors, ultrasonic velocity and salinity at a constant temperature. This tool will equip engineers to apply thermodynamic properties such as osmotic pressure and internal pressure for applications at an industrial level.

Acknowledgement

This work was completed with the help of Undergraduate students of the Department of Chemical Engineering, BITS-Pilani, K.K Birla Goa Campus: Mr. Tushar Damani, Mr. Vaibhav Sridhar, Mr. Tanmay Garg and Mr. Vibhor Mittal. Dr. Anirban would like to thank the Research Initiation Grant (BPGC/RIG/2017-2018, dt. 01/08/2017) and OPERA award (FR/SCM/230117/CHE, dt. 19/08/2017) by BITS-Pilani Goa for carrying out the work. Dr. Anirban would also like to thank DST–SERB for the research grant (CRG/2018/001538 dt. 28/01/2020) for partially supporting the work.

Associated Content

Supporting information: This material is available free of charge via the Internet at <http://pubs.acs.org>.

A comparison of NaCl-solution properties with reported literature, additional plots and relations between vapour pressure and osmotic pressure, as well as a summary of thermo-acoustical parameters determined in this work.

References

- (1) Al-Zahrani, A.; Orfi, J.; Al-Suhaibani, Z.; Salim, B.; Al-Ansary, H. Thermodynamic Analysis of a Reverse Osmosis Desalination Unit with Energy Recovery System. *Procedia Eng.* **2012**, 33 (2011), 404–414.
- (2) Al-Ghouti, M. A.; Al-Kaabi, M. A.; Ashfaq, M. Y.; Da'na, D. A. Produced Water Characteristics, Treatment and Reuse: A Review. *J. Water Process Eng.* **2019**, 28 (September 2018), 222–239.
- (3) Deshmukh, A.; Boo, C.; Karanikola, V.; Lin, S.; Straub, A. P.; Tong, T.; Warsinger, D. M.; Elimelech, M. Membrane Distillation at the Water-Energy Nexus: Limits,

- Opportunities, and Challenges. *Energy Environ. Sci.* **2018**, *11* (5), 1177–1196.
- (4) Mohammadi, A. H.; Richon, D. Thermodynamic Modeling of Salt Precipitation and Gas Hydrate Inhibition Effect of Salt Aqueous Solution. *Ind. Eng. Chem. Res.* **2007**, *46* (14), 5074–5079.
- (5) Wilczek-Vera, G.; Vera, J. H. On the Predictive Ability of the New Thermodynamics of Electrolyte Solutions. *Ind. Eng. Chem. Res.* **2009**, *48* (13), 6436–6440.
- (6) Srivastava, S. C.; Berkowitz, N. On the Relationship between Internal Pressure and Ultrasonic Velocity. *Can. J. Chem.* **1963**, *41* (7), 1787–1793.
- (7) Garver, M. M. On the Relation of Osmotic Pressure to the Intrinsic Pressure of Liquids. **1944**, *2* (September), 478–502.
- (8) Yasmin, M.; Singh, K. P.; Parveen, S.; Gupta, M.; Shukla, J. P. Thermoacoustical Excess Properties of Binary Liquid Mixtures - A Comparative Experimental and Theoretical Study. *Acta Phys. Pol. A* **2009**, *115* (5), 890–900.
- (9) Agudelo-Vera, C.; Avvedimento, S.; Boxall, J.; Creaco, E.; de Kater, H.; Di Nardo, A.; Djukic, A.; Douterelo, I.; Fish, K. E.; Iglesias Rey, P. L.; Jacimovic, N.; Jacobs, H. E.; Kapelan, Z.; Martinez Solano, J.; Montoya Pachongo, C.; Piller, O.; Quintiliani, C.; Ručka, J.; Tuhovčák, L.; Blokker, M. Drinking Water Temperature around the Globe: Understanding, Policies, Challenges and Opportunities. *Water* **2020**, *12* (4), 1049.
- (10) Chapman, M.; Tiffenbach, A.; Leitz, F. Variable Salinity Desalination. *Desalination and Water Purification Research and Development Report*; 2014.
- (11) Loutatidou, S.; Arafat, H. A. Techno-Economic Analysis of MED and RO Desalination Powered by Low-Enthalpy Geothermal Energy. *Desalination* **2015**, *365*, 277–292.
- (12) Youssef, P. G.; Al-Dadah, R. K.; Mahmoud, S. M. Comparative Analysis of Desalination Technologies. *Energy Procedia* **2014**, *61*, 2604–2607.
- (13) Semiat, R. Energy Issues in Desalination Processes. *Am. Chem. Soc.* **2008**, *42* (22), 8193–8201.
- (14) Straub, A. P.; Deshmukh, A.; Elimelech, M. Pressure-Retarded Osmosis for Power Generation from Salinity Gradients: Is It Viable? *Energy Environ. Sci.* **2016**, *9* (1), 31–48.
- (15) Singh, S.; Talukdar, M.; Dash, U. N. Studies on Molecular Interactions in Aqueous and Aqueous Urea Systems of Paracetamol (N-(4-Hydroxyphenyl) Ethanamide). *J. Mol. Liq.* **2018**, *265*, 679–686.
- (16) Chaudhary, N.; Nain, A. K. Densities, Ultrasonic Speeds, Viscosities, Refractive Indices, and Excess Properties of 1-Butyl-3-Methylimidazolium Tetrafluoroborate + N-Methylacetamide Binary Mixtures at Different Temperatures. *J. Chem. Eng. Data* **2019**, *65* (4), 1447–1459.
- (17) Hall, L. The Origin of Ultrasonic Absorption in Water. *Phys. Rev.* **1948**, *73* (7), 775–781.
- (18) Saxena, I.; Pathak, R.; Kumar, V.; Devi, R. Introduction of Ultrasonic Interferometer and Experimental Techniques for Determination of Ultrasonic Velocity, Density,

- Viscosity and Various Thermodynamic Parameters. *Int. J. Appl. Res.* **2015**, *1* (9), 562–569.
- (19) Miller, A. A. “Free Volume” and the Viscosity of Liquid Water. *J. Chem. Phys.* **1963**, *38* (7), 1568–1571.
- (20) Jacobson, B. Ultrasonic Velocity in Liquids and Liquid Mixtures. *J. Chem. Phys.* **1952**, *20* (5), 927–928.
- (21) Dey, R.; Kumar, P. A Temperature Variant Thermo-Acoustical Approach for Computation of Excess Non-Linearity Parameter and Available Volume of Binary Liquid Mixtures. *Acta Acust. united with Acust.* **2011**, *97* (1), 8–13.
- (22) Bjørnø, L. Introduction to Nonlinear Acoustics. *Phys. Procedia* **2010**, *3* (1), 5–16.
- (23) Bjørnø, L. Characterization of Biological Media by Means of Their Non-Linearity. *Ultrasonics* **1986**, *24* (5), 254–259.
- (24) Dunn, F.; Law, W. K.; Frizzell, L. A. Nonlinear Ultrasonic Wave Propagation in Biological Materials. **2008**, 527–532.
- (25) Law, W. K.; Frizzell, L. A.; Dunn, F. Determination of the Nonlinearity Parameter B/A of Biological Media. *Ultrasound Med. Biol.* **1985**, *11* (2), 307–318.
- (26) Prieur, F.; Näsholm, S. P.; Austeng, A.; Tichy, F.; Holm, S. Feasibility of Second Harmonic Imaging in Active Sonar: Measurements and Simulations. *IEEE J. Ocean. Eng.* **2012**, *37* (3), 467–477.
- (27) Narendra, K.; Kavitha, C.; Krishna, T. S. Computation of Available Volume and Non-Linearity Parameter in Liquid Mixtures Using Thermoacoustic and Thermodynamic Parameters. *Int. J. Ambient Energy* **2019**, 1–7.
- (28) Douhert, G.; Khadir, A. Thermodynamic Characterization of the Water + Methanol System, at 298.15K. *Thermochim. Acta* **1989**, *142*, 219–243.
- (29) Ahmed, K. Thermodynamic Studies of Ternary Liquid Mixtures: Application of Flory Theory to Certain Mixtures Containing Benzene+Chlorobenzene at 25° C, Sri Krishnadevaraya University, India, 2000.
- (30) Buehler, R. J.; Wentorf, R. H.; Hirschfelder, J. O.; Curtiss, C. F. The Free Volume for Rigid Sphere Molecules. *J. Chem. Phys.* **1951**, *19* (1), 61–71.
- (31) Suryanarayana, C. Measurement of Internal Pressure in Liquid Systems. *Indian J. Chem.* **1986**, *25*, 538–540.
- (32) Marcus, Y. Internal Pressure of Liquids and Solutions. *Chem. Rev.* **2013**, *113* (8), 6536–6551.
- (33) Williams, M. L. CRC Handbook of Chemistry and Physics, 76th Edition. *Occup. Environ. Med.* **1996**, *53* (7), 504–504.
- (34) Greenspan, M.; Tschiegg, C. E. Speed of Sound in Water by a Direct Method. *J. Res. Natl. Bur. Stand. (1934)*. **1957**, *59* (4), 249.
- (35) Singh, B. . Temperature Effect on Ultra-Sonic Velocity in Water. *Nature* **1945**, *156* (3967).
- (36) Bharmoria, P.; Gupta, H.; Mohandas, V. P.; Ghosh, P. K.; Kumar, A. Temperature

- Invariance of NaCl Solubility in Water: Inferences from Salt-Water Cluster Behavior of NaCl, KCl, and NH₄Cl. *J. Phys. Chem. B* **2012**, *116* (38), 11712–11719.
- (37) Marks, G. W. Dependence of Acoustic Velocity in Some Aqueous Hydroxide Solutions on Temperature and Concentration. *J. Acoust. Soc. Am.* **1959**, *31* (6), 848–848.
- (38) Zubov, A. V.; Zubov, K. V.; Zubov, V. A. Mechanism of Sodium Chloride Dissolving in Water and the Process of the Solution Aging. *Russ. J. Appl. Chem.* **2007**, *80* (7), 1249–1255.
- (39) Podolsky, R. J. The Structure of Water and Electrolyte Solutions. *Lect. Rev. Ser. Nav. Med. Res. Inst.* **1960**, *60* (5), 235–245.
- (40) Frank, H. S.; Evans, M. W. Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *J. Chem. Phys.* **1945**, *13* (11), 507–532.
- (41) Kharakoz, D. P. Chapter 7 Chain-Ordering Phase Transition in Bilayer: Kinetic Mechanism and Its Physicochemical and Physiological Implications. In *Membrane Science and Technology*; Elsevier Masson SAS, 2003; Vol. 7, pp 239–268.
- (42) Van't Hoff, J. The Function of Osmotic Pressure in the Analogy between Solutions and Gases. *Proc. Phys. Soc. London* **1887**, *9* (1), 307–334.
- (43) Zhou, W.; Song, L. Experimental Study of Water and Salt Fluxes through Reverse Osmosis Membranes. *Environ. Sci. Technol.* **2005**, *39* (9), 3382–3387.
- (44) Choi, Y.; Naidu, G.; Nghiem, L. D.; Lee, S.; Vigneswaran, S. Membrane Distillation Crystallization for Brine Mining and Zero Liquid Discharge: Opportunities, Challenges, and Recent Progress. *Environ. Sci. Water Res. Technol.* **2019**, *5* (7), 1202–1221.
- (45) Aruna, P. Studies on Physico Chemical Properties in Relation to Internal Pressure and Free Volume in Aqueous Solutions, Anna University, Madras, India, 1991.
- (46) Dack, M. R. J. The Importance of Solvent Internal Pressure and Cohesion to Solution Phenomena. *Chem. Soc. Rev.* **1975**, *4* (2), 211–229.
- (47) Mistry, K. H.; Lienhard, J. H. Generalized Least Energy of Separation for Desalination and Other Chemical Separation Processes. *Entropy* **2013**, *15* (6), 2046–2080.
- (48) Nayar, K. G.; Sharqawy, M. H.; Banchik, L. D.; Lienhard, J. H. Thermophysical Properties of Seawater: A Review and New Correlations That Include Pressure Dependence. *Desalination* **2016**, *390*, 1–24.
- (49) He, W.; Wang, Y.; Shaheed, M. H. Energy and Thermodynamic Analysis of Power Generation Using a Natural Salinity Gradient Based Pressure Retarded Osmosis Process. *Desalination* **2014**, *350*, 86–94.
- (50) Nam, D. H.; Choi, K. S. Tandem Desalination/Salination Strategies Enabling the Use of Redox Couples for Efficient and Sustainable Electrochemical Desalination. *ACS Appl. Mater. Interfaces* **2019**, *11* (42), 38641–38647.
- (51) Gabriel, K. J.; El-Halwagi, M. M.; Linke, P. Optimization across the Water-Energy

- Nexus for Integrating Heat, Power, and Water for Industrial Processes, Coupled with Hybrid Thermal-Membrane Desalination. *Ind. Eng. Chem. Res.* **2016**, *55* (12), 3442–3466.
- (52) Olkis, C.; Dong, H.; Brandani, S.; Santori, G. Ionogels at the Water-Energy Nexus for Desalination Powered by Ultralow-Grade Heat. *Environ. Sci. Technol.* **2020**, *54* (6), 3591–3598.
- (53) Kim, B. J.; Piao, G.; Kim, S.; Yang, S. Y.; Park, Y.; Han, D. S.; Shon, H. K.; Hoffmann, M. R.; Park, H. High-Efficiency Solar Desalination Accompanying Electrocatalytic Conversions of Desalted Chloride and Captured Carbon Dioxide. *ACS Sustain. Chem. Eng.* **2019**, *7* (18), 15320–15328.
- (54) Gao, J.; Guo, W.; Feng, D.; Wang, H.; Zhao, D.; Jiang, L. High-Performance Ionic Diode Membrane for Salinity Gradient Power Generation. *J. Am. Chem. Soc.* **2014**, *136* (35), 12265–12272.
- (55) Guo, Y.; Huang, H.; Li, Z.; Wang, X.; Li, P.; Deng, Z.; Peng, X. Sulfonated Sub-Nanochannels in a Robust MOF Membrane: Harvesting Salinity Gradient Power. *ACS Appl. Mater. Interfaces* **2019**, *11* (38), 35496–35500.
- (56) Merz, C. R. Physicochemical and Colligative Investigation of α (Shrimp Shell)- And β (Squid Pen)-Chitosan Membranes: Concentration-Gradient-Driven Water Flux and Ion Transport for Salinity Gradient Power and Separation Process Operations. *ACS Omega* **2019**, *4* (25), 21027–21040.

254x190mm (96 x 96 DPI)