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Is lithium brine water?

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HIGHLIGHTS

- The rapid expansion of applications of Lithium-ion batteries has raised Li demand.
- Overexploitation of Li brine resources such as Salar de Atacama raised concerns.
- There is an ongoing debate over the definition of Lithium brine as water or minerals.
- The debate has frustrated basic measures for moving towards a sustainable operation.
- Here, we used a molecular level approach to prove that the brine is a type of water.

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ABSTRACT

With the development of light and rechargeable batteries for electric vehicles, global demand for lithium has increased considerably in recent years. This has drawn more attention to how lithium is produced, especially on primary extraction operations such as those at the Salar de Atacama in Northern Chile. There are concerns that brine extraction at the Atacama could irreversibly damage the basin's complex hydrological system. However, differing opinions over the definition of water have frustrated basic action measures for minimizing impacts of operations like these. Some lithium industry stakeholders have historically described brine as a mineral, while others emphasize that brine is also a type of water in a complex network of different water resources. In this communication, we show that brines are undeniably a type of water. We support this position by investigating brine's water molecular structure using molecular dynamics simulations and comparing Gibbs formation energy of the brine using thermodynamic principles. Molecular dynamics show that the structure of water molecules in brine is similar to the structure of molecules in pure water at a pressure of 1.2 atm. The analysis of Gibbs formation energy shows that more than 99% of the brine's formation energy is directly from water, not dissolved minerals.

1. Introduction

The world is increasingly in need of lithium chemicals to make batteries in electric vehicles for decarbonization. This has increased pressure on the natural resources that host this valuable metal. Primary lithium resources can be broken down into ores and brines, while secondary resources include spent lithium-ion batteries and electronic wastes [1]. Brines such as those found at the Salar de Atacama, one of the leading lithium production sites globally, accounts for approximately 25% of today's lithium supply globally. The brine contains around 25% of salt and 75% water by mass, and is pumped from

underground into shallow man-made ponds where the water is evaporated. The evaporative process takes between 9 and 14 months, during which time several types of salt can be extracted at the different evaporation stages. Lithium chloride concentrate is then transported to a chemical plant where residual quantities of undesirable components are removed. Finally lithium carbonate and lithium hydroxide monohydrate products are made from purified lithium chloride. These are the lithium chemicals are sold to today's battery cathode manufacturers.

Evaporative processing of brines has provoked criticism from indigenous communities, researchers, environmentalists, lithium buyers, and lithium project investors [2]. They are concerned about the

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loss of water from these resources, the risks of irreversible impacts incurred to the region's ecosystem, and the impact on the wellbeing of nature and the original owners of the land [3]. Operators there extract brine from the salar and return only a fraction of the fluid to the aquifers, so most of the water is lost in evaporative processing. This draw-down of the brine from salars without human-engineered recharge causes a downward pressure gradient, or a drop in the height of brines in the aquifers. This may cause other, less salty aqueous resources to preferentially infiltrate into the salar due to this draw-down, affecting nearby lagoons that animals, plants, and humans depend on. The Gravity Recovery and Climate Experiment (GRACE) data show a declining trend in the total volume of water stored in the area. This means that the total water output volume is more than its input [4] and the basin has no chance of recovery [3]. Under such conditions, large quantities of water are lost to the atmosphere every year to process the brines into lithium chloride concentrates, with unsustainable return to the aquifer [5,6]. This is potentially evidenced by the decline in vegetation in the region over the last 20 years [3]. These conditions are causing the damping capacity of salt flat nucleus to be lost [6].

In some brinefields, the efforts to address the environmental issues have been hindered since the brine is not considered "water", but instead regulated like it was a mineral [3]. The most commonly presented reasoning behind this is that humans cannot drink brine without suffering acute health issues, and it is not economically viable to use brine to make freshwater for agriculture. According to the World Health Organization, water having a total dissolved solids (TDS) value of greater than 1,200 mg/kg is unacceptable for direct consumption by humans [7], while brines can contain around 25% by mass, or 250,000 mg/kg of salt. In Nevada, USA, for example, the government classifies lithium brine as a type of water, but geothermal water from deeper down is not regulated as water consumption, partly because the water is re-injected. Many water resources are not drinkable, but they are also part of the earth's water cycle. Moreover, high TDS water is a conventional concept in many industries such as shale oil and gas extraction, flash steam geothermal systems, and CO₂ storage sites in which it is still called water [8].

Considering brine a type of water could have environmental complications particularly if that requires the industry to employ energy-intensive zero water loss technologies for lithium extraction from brines. A separate study is required to identify and compare the environmental complications of current technologies considering brine as minerals or water. Emerging advanced direct lithium extraction (DLE) technologies with a low carbon footprint could be helpful to target and extract only Li ions or LiCl molecules from the brine while returning the Li-free brine to the aquifer. Modern DLE technologies use selective sites in engineered materials such as adsorption media, ion-exchange materials, electrochemical approaches, or embedded in advanced nanofiltration membranes, which could enable lithium extraction from brines with the opportunity to return almost all the brine to the salar's aquifers. Recent reports revealed that the energy consumption of these technologies could be substantially reduced [9].

Since the brine-water nexus conversation influences the way we understand environmental impacts, it is pivotal to fundamentally understand if brine should be considered a type of water, mineral, or both. Here, we share a view that brine should be considered a type of water by looking at the topic from first principles physiochemistry and thermodynamics. We use molecular dynamic (MD) simulations to support our position. We hope that this paper will be helpful for thinking through the environmental impacts of lithium brine extraction and impacts on water resources, and to give regulators, investors, and buyers tools for thinking about this complex topic. Working with the proper definition of brine as water is critical for ensuring that the impacts of lithium extraction feeding the electric vehicle battery industry are minimized, and not seen as more severe than the impacts of climate change: the problem we are trying to solve in the first place.

2. Water and saline solutions

The water molecule contains two hydrogen atoms and one oxygen atom, bonded together by covalent bonds. Hydrogen atoms have a positive charge and are oriented at an angle of about 104.5 degrees around the oxygen atom, which polarizes the water molecule bonds. Under standard atmospheric conditions, water with a molecular weight of 18.015 g/mol should be in gaseous form instead of a liquid state [10]. This unusual behaviour is due to the hydrogen bonds that hydrogen atoms form with non-bonding electrons of the oxygen atom in another water molecule. Hydrogen atoms are continuously exchanged among water molecules because of the protonation/deprotonation processes [11]. In this way, the liquid water structure is constantly breaking and regenerating, contributing to water surface tension and high viscosity.

In pure water, hydrogen bonds cause each water molecule to be normally associated with the other four molecules in a tetrahedral arrangement [11]. Pure water is odourless, colourless, and tasteless to humans and is not electrically conductive. What makes water a substance critical to life on Earth is its high potential as a solvent. Many nutrients and vital elements reach cells through aqueous solutions. Also, vital chemical reactions of living organisms occur in aqueous solutions. Salts are the major solutes in water and are present in varying concentrations. Drinking water, brackish waters, ocean water, and of course high TDS waters each have a role to play in the Earth's water cycle and the life of living things. Besides taste, salinity in water affects other properties. As shown in Fig. 1, increasing the salinities of solutions change their physicochemical parameters, i.e., density, refractive index, electrical conductivity, viscosity, and freezing temperature [13]. However, as stated below, the fundamental concept of water does not change at different degrees of salinity; its properties change continuously.

The high polarity of the water molecule is responsible for the solubility of ionic compounds like salts in water. During the dissolution of an ionic solid in water, the substance is divided into separate anions and cations. The anions attract the positive charge while the cations attract the negative charge of the water molecules. For example, when sodium chloride dissolves in water, four water molecules surround the sodium ion, called the hydration shell. The structure of water molecules around the hydration shell is disturbed by the presence of other ions, which is called the partially ordered region of the hydration shell [14].

The presence of different ions in the brine affects the structure of water and changes its physical properties. Nevertheless, water's molecular structure is still stable, although it differs from pure water's molecular structure. A high concentration of ions in solutions can disrupt the characteristic tetrahedral structure of water molecules, similar to the perturbing effect of pressure and temperature. For example, the hydrogen-hydrogen partial structure between water molecules in a four molal solution of sodium chloride is similar to that of pure water at a relative pressure of 1.4 atm [15]. Therefore, as water under high pressure or temperature is still called water, water that has dissolved large amounts of salt is still water.

3. Molecular dynamic simulation

Molecular dynamic simulations can help clarify this situation. In this study, Salar de Atacama brine (described in Table 2) was simulated as well as pure water in five different pressures of 1.0, 1.1, 1.2, 1.3, and 1.5 atm. For all cases, the temperature is assumed to be 298 °K. The ions were designed using PyMOL software and then optimized [16,17]. Their topology was calculated using the LigParGen server, and their charges were calculated using density functional theory (DFT) by quantum espresso software. Molecular simulations were then implemented using GROMACS. The simulations were performed using the Parrinello-Rahman dynamics method [18,19] and Nosé-Hoover thermostat algorithms [20,21] with a cut-off radius of 2 nm. The TIP3P water model and "the all-atom optimized potentials for liquid simulations (OPLS-AA) force field" have also been adopted. To approve the stability of the

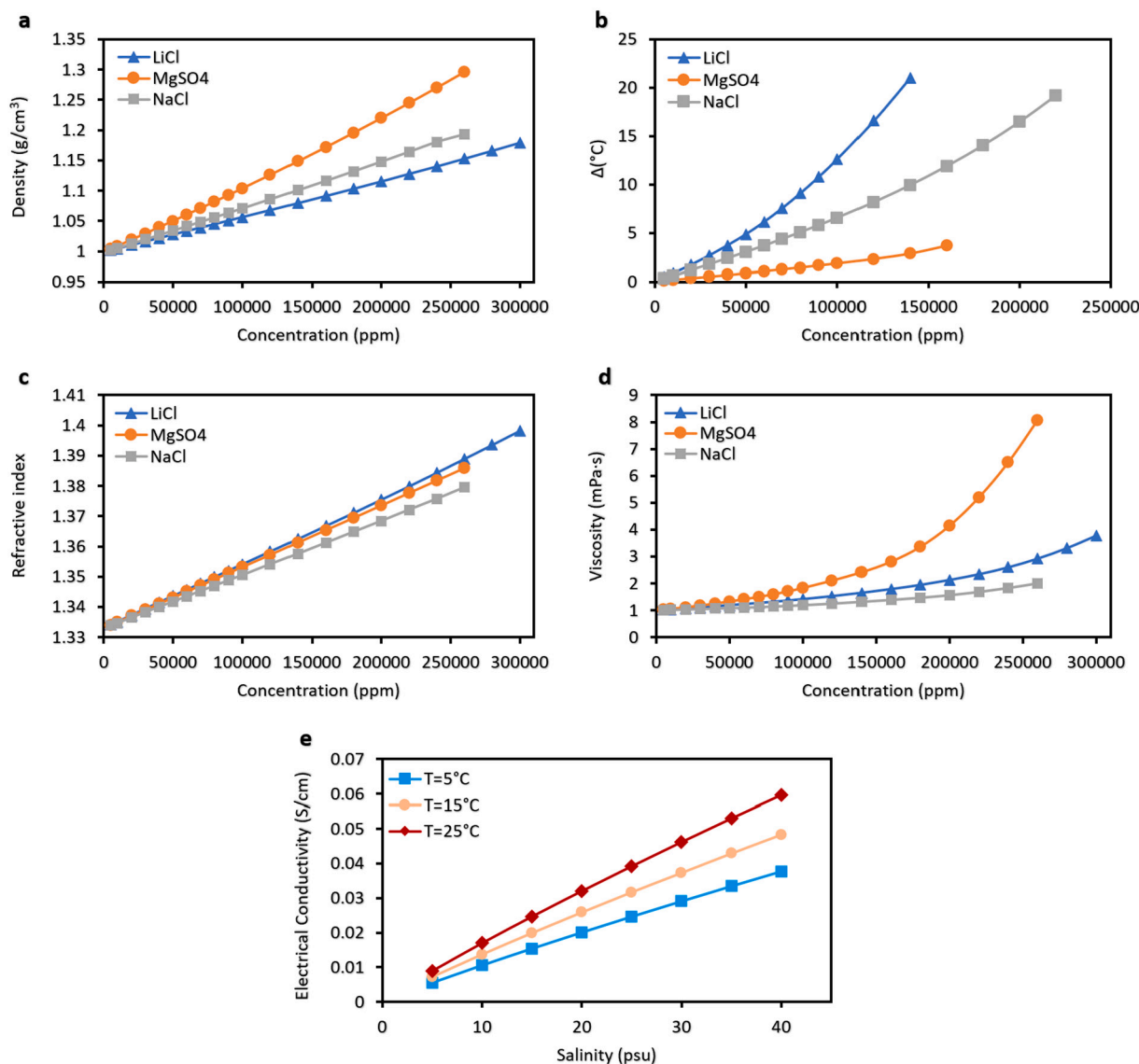


Fig. 1. (a) density and (b) freezing point depression (c) refraction index, relative to the air, at a wavelength of 589 nm, (d) absolute viscosity of three well-known aqueous solutions as a function of concentration [12] and (e) electrical conductivity of seawater relative to salinity in different temperatures (1 psu is about to 1000 ppm) [13].

simulation, the root mean square deviation (RMSD) of atoms in all the cases is done.

To analyze the bonding angles and lengths, water molecules were randomly selected from ionic solution, and their average parameters were considered. As shown in Fig. 2a, high pressure has changed the atomic forces and reduced the H-O-H bonding angle. A similar trend has been followed in brine, where the bonding angles are reduced due to water molecules' interaction with ions under their atomic forces' influence. The bonding angle of a water molecule in the typical brine is approximately equal to pure water's bonding angle at a pressure of 1.2 atm. Likewise, the O—H bonds' length in the water molecule also increases in the brine, which is approximately equal to the O—H bond length in pure water under 1.2 atm pressure (Fig. 2b). Even the structure of molecules attached to ions is not significantly different from pure pressurized water. This has been attributed to the partial molar volumes of the respective salts, which could induce a substantial electrostrictive effect on water structure by distorting the hydrogen-bonded network of water [15]. Tromp and Neilson found out that in a high LiCl solution (e. g. 10 m) the number of hydrogen bonds is about 70% lower than in pure water [22]. They also realized that the intermolecular water structure in

the LiCl solution is substantially affected by the presence of ions while the intramolecular water structure is not distinguishable from that of pure water. The effect of each ion on the structure of the attached water molecule can be found in Table 1.

This is not the only similarity between the brine and pure water under pressure. As shown in Fig. 2c, the average entropy of separated atoms in brine is close to pure water's entropy at 1.2 atm, which means the atomic irregularity of water molecules is almost the same in both cases. Moreover, radial distribution function (RDF) analysis was performed to analyze the radial distribution of hydrogen bonds. This analysis determines the dispersion of hydrogen bonds at different points in the solution simulation box. The RDF here shows the probability density of hydrogen bonds, and the higher the value at one point in the box, the greater the number of hydrogen bonds at that point. The maximum point of RDF represents the highest aggregation of hydrogen bonds, illustrated in Fig. 2d for the brine and pure water at different pressures. Almost equal maximum RDF shows another similarity between the brine and water under 1.2 atm pressure in hydrogen bond distribution. Furthermore, Fig. 2e shows another similarity between brine and pure water under 1.2 atm pressure because the number of

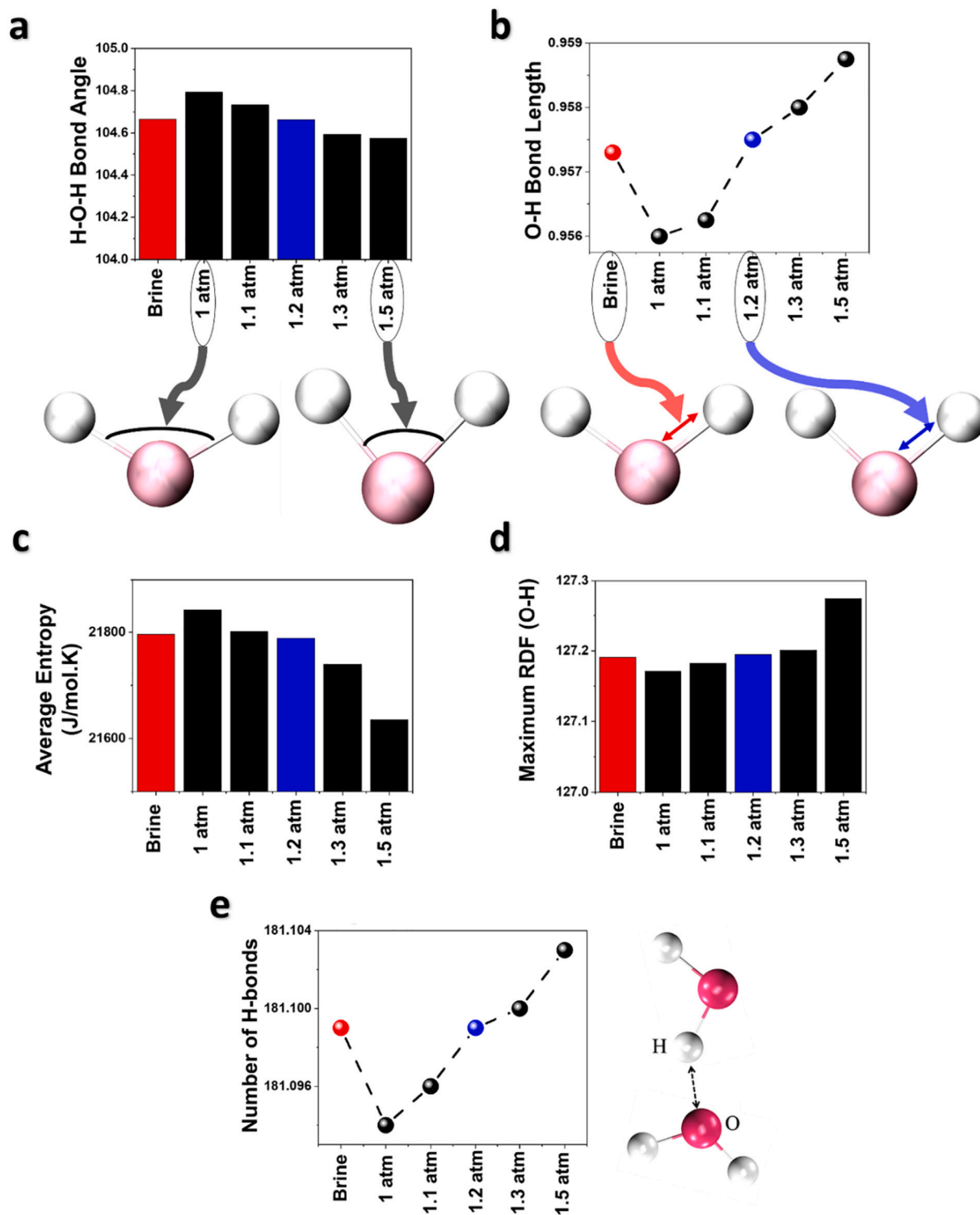


Fig. 2. Comparison of molecular properties for pure water at different pressures and typical brine (a) H-O-H bond angle. (b) O—H bond length (c) Average entropy (d) maximum RDF between O and H (e) Average hydrogen bonds number.

Table 1

H-O-H bond angle and O—H bond length of water molecules neighbouring ions in the brine.

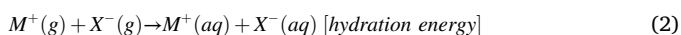
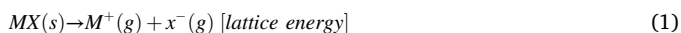
	Na ⁺	K ⁺	Mg ²⁺	Li ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	B/	HCO ₃ ⁻
H-O-H bond angle (°)	104.68	104.754	104.761	104.687	104.783	104.789	104.799	104.741	104.804
O-H bond length (Å)	0.9571	0.9583	0.9584	0.9573	0.9587	0.9604	0.9617	0.9571	0.9619

hydrogen bonds is about equal.

Fig. 3 shows the surface charge density of the atoms in a water molecule in three states. Compare to pure water at ambient pressure, both pure water under 1.2 atm pressure and the brine show a slightly more negative charge. Therefore, it can be concluded that the effect of the ionic solution on the surface charge of atoms is similar to the effect of increasing pressure.

4. Thermodynamics of solutions and minerals

When polar solids dissolve in water, the ion crystal bonds and some hydrogen bonds of the water structure also break down, which consumes lattice energy, i.e., is endothermic. The resulting ions interact with water molecules, producing energy called hydration energy, i.e., is exothermic. Eqs. (1) and (2) show the process of dissolving the hypothetical salt MX. The balance of this energy production and consumption determines whether the dissolution process is net exothermic or endothermic and the direction of enthalpy changes.



$$H_{\text{solution}} = H_{\text{hydration}} + H_{\text{lattice energy}} \quad (3)$$

Similarly, the dissolution process both increases and decreases the disorder in the molecules. The immobile ions in the solid start to move randomly within the solution, while the solvent molecules form bonds with the ions. This balance is intensifying the state of disorder, which consequently increases the entropy of the system. When the salt dissolves, the entropy increase is such that the Gibbs free energy change will always be negative, even if the enthalpy change is positive (Eq. (4)). This implies the fact that the formation of solid salt never happens spontaneously.

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

The use of Gibbs free energy has allowed us to describe the states and structures of materials [23]. The average composition of brine in the Salar de Atacama with the Gibbs formation energy of each relative to the pure solid-state is given in Table 2, where the total salinity is 332.3 g/L. If we add the Gibbs formation energy for lithium-ion and chloride-ion together, it is equal to -425 kJ/mol, while this value for solid lithium chloride is equal to -386 kJ/mol. This difference indicates that the formation of solid lithium chloride from ions in the brine does not occur by itself and requires energy. Similarly, other ions in the brine have lower formation energies than their corresponding salts. Among these, it is only for water that the formation energy is not significantly different from the standard state. It should be noted that the slight variation is due to the temperature difference. In other words, according to standard

Gibbs free energy of formation, the water molecule is the only molecule in brine that is already in a standard state and does not need to change for a pure stable state.

Gibbs free energy for 1 kg of the brine can be obtained from the following equations:

$$G \equiv \sum_i n_i \mu_i \quad (5)$$

$$\mu_i \equiv \mu_i^\circ + RT \ln a_i \quad (6)$$

$$a_i = x_i \gamma_i \quad (7)$$

where the x_i is the mole fraction of the substance and γ_i is individual activity coefficients of the ion in water, the total Gibbs formation energy is calculated as $-11,552.6$ kJ/kg such that 83.1% of the total Gibbs free energy originates from water molecules (-9624.28 kJ) and 15.8% (-1820.4 kJ) is due to ion-water bonds between water molecules and monoatomic ions including Na^+ , K^+ , Mg^{2+} , Li^+ , Ca^{2+} and Cl^- . Complex ions such as SO_4^{2-} and HCO_3^- , make up less than 0.9% (-107.9 kJ) of the total formation energy. Therefore, water originally or directly affects 99.1% of the formation energy in brine. Since water contains almost all the Gibbs formation energy in brine, thermodynamically, brine should be considered a type of water.

5. Conclusion

The results of molecular dynamics simulations in terms of bonding angles and lengths, average entropy of separated atoms, RDF, number of hydrogen bonds, and surface charge density show that the brine's water molecules are similar to pure water at a pressure of 1.2 atm as it is at 1 atm. Therefore, just as pressurized water is still called water, so is brine, since there is no thermodynamic phase demarcation between the two. On the other hand, the contribution of water with more than 99% of the Gibbs formation energy of brine shows the complete dominance of water in the brine's formation energy. The definition of brine as a mineral has fundamental flaws as opposed to a type of water. Instead, brine is a type of water containing minerals. We hope that our analysis of brine and water from a fundamental thermodynamics perspective and the molecular level phenomena provides a scientific context for regulators, investors and other stakeholders when thinking about this topic.

New frameworks for quantifying the value of water in financial calculations should be pursued for making complex decisions about water and brine use. As long as globally satisfying information on groundwater aquifers' hydrogeological behaviour in salars is not public, conservative approaches like the precautionary principle will be relied on for making decisions around brine use in development programs. DLE technologies could also play a major role in maximizing the production of lithium from brines around the world. The extraction of lithium from

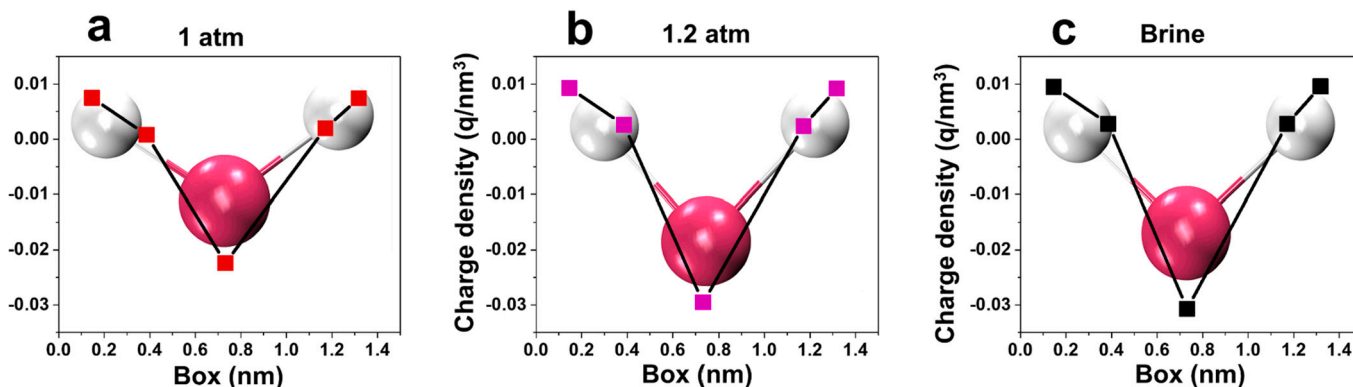


Fig. 3. Charge distribution of water molecules at different pressure as well as in the presence of ions. (a) pure water at 1 atm pressure. (b) pure water at 1.2 atm pressure. (c) typical brine.

Table 2
Average composition and Gibbs formation energy of typical brine of the Salar de Atacama.

	Na ⁺	K ⁺	Mg ²⁺	Li ⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	B/	HCO ₃ ⁻	H ₂ O	Total
Typical Composition of Brine (g/kg _{brine}) [8]	74.16	19.23	7.86	1.28	0.37	154.44	12.96	0.36	0.19	729.14	1000.00
Gibbs Free Energy at Standard State, μ° (kJ/mol) [12]	-261.88	-283.26	-454.8	-293.3	-553.54	-131.3	-774.5	-0.00	-586.85	-237.14	
individual activity coefficients of ions, γ_i [24]	0.84	0.899	0.79	0.97	0.9	0.78	0.74	-	0.97		
Partial Gibbs Free Energy, G_i (kJ/kg _{brine})	-867.0	-144.3	-151.2	-57.1	-5.2	-594.9	-106.0	-0.7	-1.9	-9624.3	-11,552.6

brine resources in South America will play a vital role in decarbonization and tackling climate change. However, we believe that increased transparency, accurate evaluation of environmental impacts, respect for the rights of the original owners of the land, and the use of advanced technologies all have an essential role to play in building a better battery value chain.

CRediT authorship contribution statement

Mojtaba Ejeian: Writing- original draft preparation.

Alex Grant: Writing, concept developing, discussion.

Ho Kyong Shon: Reviewing and editing.

Amir Razmjou: Reviewing and Editing, Leading, concept developing, simulation.

Declaration of competing interest

Amir Razmjou on behalf of authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] P. Moazzam, et al., Lithium bioleaching: an emerging approach for the recovery of Li from spent lithium ion batteries, *Chemosphere* 277 (2021), 130196.
- [2] W. Cha-umpong, et al., Concentrating brine for lithium recovery using GO composite pervaporation membranes, *Desalination* 500 (2021), 114894.
- [3] I. Garcés, G. Alvarez, *Water Mining and Extractivism of the Salar de Atacama, Chile* 245, 2020, pp. 189–199 (2020-July).
- [4] W. Liu, D.B. Agusdinata, Interdependencies of lithium mining and communities sustainability in Salar de Atacama, Chile, *J. Clean. Prod.* (2020) 260.
- [5] L.A. Munk, et al., *Hydrogeologic and Geochemical Distinctions in Salar Freshwater Brine Systems*, 2020.
- [6] M.A. Marazuela, et al., Towards more sustainable brine extraction in salt flats: learning from the Salar de Atacama, *Sci. Total Environ.* (2020) 703.
- [7] J. Fawell, U. Lund, B. Mintz, *Total Dissolved Solids in Drinking-water. Background Document for Development of WHO Guidelines for Drinking-Water Quality*, World Health Organization, Geneva, 2003.
- [8] C.F. Baspineiro, J. Franco, V. Flexer, Potential water recovery during lithium mining from high salinity brines, *Sci. Total Environ.* (2020) 720.
- [9] G. Liu, Z. Zhao, A. Ghahreman, Novel approaches for lithium extraction from salt-lake brines: a review, *Hydrometallurgy* 187 (2019) 81–100.
- [10] D. Eisenberg, W. Kauzmann, W. Kauzmann, *The Structure and Properties of Water*, Oxford University Press on Demand, 2005.
- [11] X.-F. Pang, *Water: Molecular Structure and Properties*, World Scientific, 2014.
- [12] J.G. Speight, *Lange's Handbook of Chemistry*, McGraw-Hill, 2004.
- [13] D.R. Lide, *CRC Handbook of Chemistry and Physics vol. 85*, CRC Press, 2004.
- [14] A. Razmjou, et al., Design principles of ion selective nanostructured membranes for the extraction of lithium ions, *Nat. Commun.* 10 (1) (2019).
- [15] R. Leberman, A.K. Soper, Effect of high salt concentrations on water structure, *Nature* 378 (6555) (1995) 364–366.
- [16] A.F. Rodrigues-Oliveira, et al., Evaluation of common theoretical methods for predicting infrared multiphotonic dissociation vibrational spectra of Intramolecular hydrogen-bonded ions, *ACS Omega* 3 (8) (2018) 9075–9085.
- [17] T. Wang, G. Brudvig, V.S. Batista, Characterization of proton coupled electron transfer in a biomimetic oxomanganese complex: evaluation of the DFT B3LYP level of theory, *J. Chem. Theory Comput.* 6 (3) (2010) 755–760.
- [18] A. Muralidharan, et al., Molecular dynamics of lithium ion transport in a model solid electrolyte interphase, *Sci. Rep.* 8 (1) (2018) 10736.
- [19] E. Alimohammadi, et al., Graphene-based nanoparticles as potential treatment options for Parkinson's disease: a molecular dynamics study, *Int. J. Nanomedicine* 15 (2020) 6887–6903.
- [20] T.C. Lourenço, et al., Interfacial structures in ionic liquid-based ternary electrolytes for lithium-metal batteries: a molecular dynamics study, *J. Phys. Chem. B* 124 (43) (2020) 9648–9657.
- [21] D. Sidler, S. Riniker, Fast Nosé–Hoover thermostat: molecular dynamics in quasi-thermodynamic equilibrium, *Phys. Chem. Chem. Phys.* 21 (11) (2019) 6059–6070.
- [22] R.H. Tromp, G.W. Neilson, A.K. Soper, Water structure in concentrated lithium chloride solutions, *J. Chem. Phys.* 96 (11) (1992) 8460–8469.
- [23] A.F. Lisovsky, Thermodynamics of the formation of composite material structures. A review, *J. Superhard Mater.* 37 (6) (2015) 363–374.
- [24] J. Kielland, Individual activity coefficients of ions in aqueous solutions, *J. Am. Chem. Soc.* 59 (9) (1937) 1675–1678.