

Review and new insights into the application of molecular-based equations of state to water and aqueous solutions



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ARTICLE INFO

Article history:

Received 28 September 2015

Received in revised form

13 January 2016

Accepted 14 January 2016

Available online 22 January 2016

Keywords:

Water

Aqueous mixtures

SAFT

CPA

Association models

ABSTRACT

Water is a fascinating compound, essential to our life and present in most of the biological and industrial systems. In spite of its importance, the particular features of water and the complex interactions formed when mixed with other compounds make most of the models developed up to date unable to accurately describe the phase and interfacial behavior of aqueous mixtures, unless a vast amount of experimental data are available to fit the model to particular conditions. As a consequence, several theoretical approaches have been developed over the years to reproduce the physics of water solutions with different degrees of success, depending on the underlying accuracy of the models. Among them, equations of state which explicitly account for hydrogen-bonding interactions, such as the Statistical Association Fluid Theory (SAFT) and similar approaches, are built to provide a better picture of water-systems behavior, although there is still room for improvement.

With the occasion of the 25th anniversary of the SAFT creation, we summarize here some association theories developed in the last 25 years including the association term proposed by Wertheim. Given the vast amount of works published during these years, the review focuses on the application of SAFT equations, Cubic-plus-Association (CPA) and Group Contribution plus Association (GCA) to aqueous solutions of systems with large impact at the chemical and energy industry today: binary mixtures of water with hydrocarbons, CO₂, alkanols, amines and ionic liquids. Different molecular models and approaches are revised in detail. In addition, we present new modeling data using the soft-SAFT equation, to highlight the advantages of explicitly including hydrogen bonds when building the equation, even if done at a coarse-grained level, and the remaining challenges and opportunities for improvement.

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1. Introduction

Water is probably the most fundamental building block of life on Earth, present almost everywhere. However, and despite its importance, there is not available yet a comprehensive model to accurately describe its behavior in a wide range of conditions. The apparently simple structure of water exhibits highly complex and non-ideal behavior both, as a pure fluid, and in mixtures. As a gas, water is one of the lightest known compounds; as a liquid, it is much denser than anticipated, while solid water is much lighter than expected when compared with its liquid form. Water can be extremely slippery and extremely sticky with small changes of temperature and pressure.

Up to now, a total of 72 physicochemical anomalies have been associated to water [1]. As an example some of the anomalous properties of liquid water related to temperature are shown in Fig. 1. Accurate knowledge of some of these properties, such as density, viscosity, compressibility or heat capacity, is essential, from the engineering point of view, for an accurate process design. It can be observed in Fig. 1 that small changes in temperature induce large modifications in the different properties. Hence, it is important to have precise values of them for the appropriate design of the specific process.

Among the known water anomalies, the one on density stands by itself for its importance for live on Earth; due to this density anomaly water expands on both, heating and cooling. This maximum in density, together with the low ice density compared to the liquid density, is responsible for (i) the need of all bulk fresh water (not just its surface) to be close to 4 °C before any freezing can occur, (ii) the freezing of rivers, lakes and oceans occurs from

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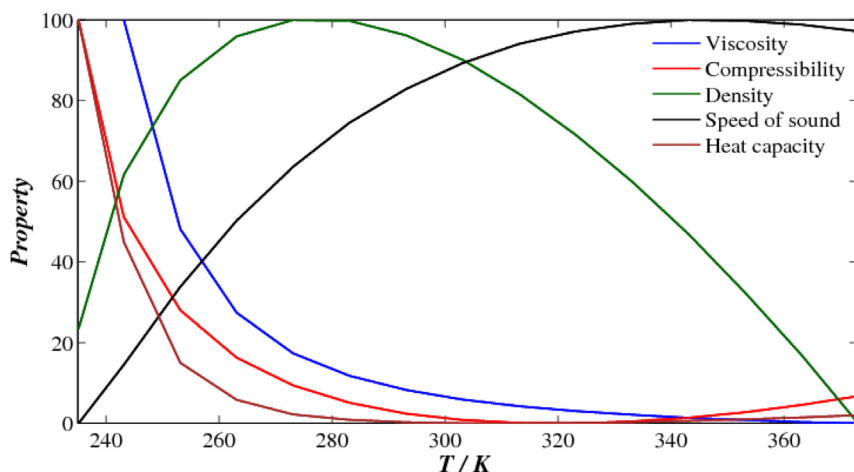


Fig. 1. Representation of some of the anomalous properties of liquid water as a function of temperature. The graph uses data that have been scaled between their maximum and minimum values within a 0–100 range. Experimental data taken from Ref. [1].

top to down, so allowing survival of the bottom ecology, insulating the water from further freezing, reflecting back sunlight into space and letting rapid thawing, and (iii) density driven thermal convection causing seasonal mixing in deeper temperate waters carrying life-providing oxygen into the depths [1].

Besides, the observed tendency of nonpolar substances to aggregate in aqueous solution and exclude water molecules (known as the hydrophobic effect), is responsible for the separation of a mixture of oil and water into its two components and the stability of cell membranes: it drives protein folding as well as the insertion of membrane proteins into the nonpolar lipid environment, and stabilizes protein-small molecule interactions, being also essential to live.

A dream for many researchers is to find models accurate enough to describe the behavior of water under different conditions; however, as mentioned, this is an arduous task. One of the main reasons for this challenge relies on the associating nature of water: hydrogen bonding is highly anisotropic, very directional and lead by short range strong attractive forces. In addition, van der Waals forces also play a subtle role at near ambient temperature conditions. Due to the presence of these forces, the description of the thermophysical properties of aqueous mixtures poses astringent tests to any modeling approach. Hence, as aqueous mixtures are found in almost all industrial and biological processes, and in spite of the developments already done, reliable tools able to provide an accurate description of the thermophysical properties still are in high demand.

The behavior of water and aqueous system has been described using different scales, depending of the degree of detail and the computational time needed. Water has been intensively studied as a pure fluid, and the bibliography shows examples from ab-initio calculations [2–3], to molecular simulations [4] and mesoscopic modeling lattice approaches [5][6], in addition to the application of empirical equations [7], classical equations of state (EoSs) [8] and molecular-based EoSs [9]. The first simulation of liquid water was published in 1969 using the Monte Carlo (MC) method [10], then followed by the molecular dynamics (MD) studies of Rahman and Stillinger in the early 70s [11–12].

As the modeling studies on water are very abundant, and so are the equivalent reviews, this work is dedicated to reviewing recent modeling approaches of water using molecular-based EoSs, i.e., equations firmly rooted on statistical mechanics and explicitly taking into account the hydrogen bond formation. An excellent and

extensive educational review on computational molecular models for simulations of water was published by Wallqvist and Mountain in 1999 [13]. Jorgensen and Tirado-Rives published an updated review on potential energy functions for water and organic systems [14]. The reader is also referred to [15] for a review on molecular simulations of supercritical water and to [16] for a comparison of non-polarizable models for ice (solid water). Furthermore, as several reviews related to SAFT developments and applications from a broad perspective have been published in the last decade [17–20], we present here a summary of the contributions published in recent years concerning the application of association molecular-based EoSs to water systems of current industrial interest, providing new and complementary information.

In addition to the review of published work on the chosen aqueous mixtures, new modeling data is presented in this contribution using the soft-SAFT EoS [21–23]. Soft-SAFT has been recently extended to calculate different properties, including accurate predictions of the critical region with a specific crossover treatment [24–26], second order thermodynamic derivative properties [27–29], interfacial [30–32] and transport properties [33–34]. It has proven to be highly accurate for several challenging systems, including water with hydrocarbons [35] and alcohols [36], blends of refrigerants [37] and aqueous ionic liquids systems [38–41]. The goal is to illustrate the performance of the equation on several examples of aqueous mixtures with hydrocarbons, carbon dioxide, amines and ionic liquids, all systems of current industrial interest for which most of the classical approaches fail. Particular attention is paid to the effect of the cross-association interactions on the phase and interfacial properties of aqueous solutions, indicating the strengths and the limitations of the approach.

In the following sections, we present some molecular-based models explicitly accounting for association, including SAFT, CPA and GCA. Section 3 is devoted to the application of these associating models to obtain key thermophysical properties of pure water, emphasizing also the molecular models and the parametrization methodologies. In section 4 we present a summary of the application of these equations to mixtures of water with non-associating fluids and water with associating compounds, where self- and crossed-association occur. The last section provides a summary and some remaining challenges and opportunities for modeling water and its mixtures with this approach.

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