A Formulation for the Relative Permittivity of Water and Steam to High Temperatures and Pressures Evolved Using Genetic Programming

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ABSTRACT

The relative permittivity (or static dielectric constant) of water and steam has been experimentally obtained from a relatively wide range of temperatures and pressures. A suite of functions for predicting the relative permittivity in four distinct thermodynamic regions is evolved using genetic programming. A data set comprised of all of the most accurate relative permittivity values, along with temperature, pressure, and density values, is used for this task. The accuracy of these functions is evaluated by comparing the values for the relative permittivity calculated using the evolved function and the values calculated using the latest formulation of Fernandez et al, to the aforementioned data set. In all regions, the newly evolved function performs comparably to or better than the most current formulation in terms of difference between calculated and experimental values for the dielectric constant. This research represents a successful application of artificial evolutionary techniques to relative permittivity prediction in physical chemistry.

Categories & Descriptors: J.2 [**Physical Sciences**]: Relative Permittivity, Genetic Programming Application.

General Terms: Algorithms, Experimentation

1. INTRODUCTION

The relative permittivity (or static dielectric constant) of water and steam has been experimentally determined for a relatively wide range of temperatures and pressures. Relative permittivity is an important indicator of the solvent behavior of water in a variety of biological (cell membrane electrophysiology, intracellular biochemical processes) and geophysical/industrial (geochemical high temperature, high pressure processes in deep sea vents and in industrial processing plants) settings.

Over the years, many researchers have worked to derive a single function that accurately predicts the relative permittivity of water and steam, the earliest of which being Quist and Marshall's 1965 formulation [3]. As research in this area progressed, work was done to explore more of the temperature and pressure spectrum, refine experimental results, and propose alternate formulations in order to enhance relative permittivity prediction.

Recently, Fernandez et al. compiled all of the experimentally available data for the relative permittivity of water and steam in a single database [1]. Furthermore, they evaluated the methods used to experimentally derive the relative permittivity and chose a subset of the total data available that represented the most accurate values and that was recommended for use in data correlation. In 1997, Fernandez et al. proposed a new formulation based on a portion of this subset [2]. Their new formulation, based on a statistical regression function, approximated the relative permittivity very well across the entire experimentally available temperature and pressure range.

The relative permittivity of a substance, ε_r, is roughly defined as the ability of a substance to transmit or allow the existence of an electric field. It is used for practical purposes, for example, in the design of capacitors. The behavior of the relative permittivity of water is related to its physical state or phase (as a liquid or as vapor), temperature, and pressure. Experimentally verified relative permittivity values for water in its solid phase (as ice) at temperatures as low as 190K ($-83°C$) exist, however these data do not include corresponding pressure values for any of the measurements. Water, in its liquid or vapor (steam) state, exists within a large range of temperatures and pressures, and this range has been traditionally divided into 4 regions, A, B, C, and D. Region A is the normal liquid water state between the normal freezing and boiling points (~273K to ~373K) at pressures up to 1000MPa. Region B refers to water along the liquid-vapor phase boundary. For water located in this region, in contrast to all other regions, every pair of temperature/pressure values takes on two density values (corresponding to the phase, either liquid or vapor/steam, in which the water occurs). Region C is the region with a temperature above 373.15K. At lower pressures and temperatures within region C, water is in the normal vapor (steam) state. At higher pressures and temperatures in this region, water becomes a supercritical fluid, that is, water ceases to behave as if it were in either the liquid or vapor state, but rather exhibits a combination of the thermodynamic properties attributable to both liquids and gases. Finally, region D refers to super cooled water (water that exists in the liquid state below the normal freezing point of 273.15K at the standard pressure of ~.1MPa).

The behavior of the relative permittivity exhibits discontinuities along the liquid-vapor phase boundary (region B) and in the supercritical part of the region above the normal boiling point (region C), with very small changes in the temperature and pressure causing very large changes in density and in the value of

the relative permittivity. As a result, theoretical formulations for calculating the relative permittivity of water have mainly focused on a broad range of temperatures (~270K to ~1000K) and a narrow range of pressures (~.1MPa to 100MPa). Furthermore, data points along the phase boundary (region B), although numerous, have not had their pressure or density values recorded, and thus have not figured in any data-driven correlations that correct for pressure and density differences. The most current formulation for approximating the relative permittivity across the entire range of experimental temperatures and pressures may be found in [2]. Their formulation uses 5 adjustable parameters and a total of 25 constants and domain specific non-adjustable parameters, and approximates well across the entire range of experimentally available values.

2. EXPERIMENTS

In our experiments, a variety of different function and terminal sets were explored in an effort to evolve a single function that could model the relative permittivity of water as a function of pressure, temperature, and density in thermodynamic regions A, C, and D of the temperature-pressure phase space. Unfortunately, no temperature *and pressure* data for region B is currently available, and thus two functions approximating the dielectric constant in region B (vapor saturation and liquid saturation) taking only temperature into account were evolved separately.

The suite of functions for regions A, B, C, and D was evolved using experimentally verified input data sets, and output results were then compared to relative permittivity values experimentally observed from the same values. These data sets were compiled from all previous experimentally available data, and were then corrected by Fernandez et al. to coincide with the most recent internationally accepted temperature scale, ITS-90. The final data set uniformly represented the dielectric constant at every temperature, pressure, and density value that was both accurate and experimentally available (as of December 2006).

3. RESULTS

The evolved functions are significantly smaller than the formulation developed by Fernandez et al. (31 terms for the regions A, C, D function, 24 terms for the liquid saturation function, and 17 terms for the vapor saturation function versus 112 terms for Fernandez et al.'s formulation) and use only three adjustable parameters (temperature, pressure, and density), zero non-adjustable domain specific parameters, and only fifteen of the one hundred possible random ephemeral constants that were available during function evolution.

The evolved function performed comparably to Fernandez et al.'s formulation in all collected statistical categories except the minimum absolute difference. However, our proposed formulation and Fernandez et al.'s formulation differ in the way each was generated. Fernandez et al. did not use the entire set of data points that they recommended for data correlation, but rather a significantly reduced subset of this total dataset (127 data points

out of the total 771 data points for all four regions). As should be expected, our formulation does not perform as well as Fernandez et al.'s on these selected data points, but does have a smaller maximum absolute difference across the data set. This dataset does not cover the entire thermodynamic space, and thus, Fernandez et al. used a variety of theoretical considerations to buttress the sparseness of their dataset. In the case of region B, Fernandez et al. also provide pressure and density values for the data points that they used in constructing their formulation, even though no experimental pressures and densities for this region exist. Furthermore, Fernandez et al. weighted each data point in their dataset differently, based on certain theoretical and experimental factors. Although it was our goal to create a formulation following steps as similar to Fernandez et al.'s as possible, we could not follow this aspect of their experimental methodology. This approach entailed creating copies of each data point in proportion to its weight and then reinserting those copies back into the data set or multiplying the error on each data point in proportion to its weight. This seems tractable until one realizes that the weights of some data points are very small. As a result, certain data points with much larger weight values would skew the evolutionary search to find functions that approximate those points well, but approximate the low-weight data points very poorly. This comes at the expense of not covering the entire thermodynamic space. Thus, we decided to leave the weights of all data points equal, and to use all of the experimental data that was available and recommended for correlation.

A suite of functions that approximate the relative permittivity of water and steam across the entire experimentally verified range of temperatures and pressures has been developed. These functions were evolved using the GP technique with a specific function and terminal set, and their accuracy has been compared to that achieved by Fernandez et al.'s most recent formulation. The evolved functions approximate the relative permittivity of water and steam extremely well, comparing favorably with Fernandez et al.'s formulation across the entire experimentally available temperature and pressure range, while being simpler computationally.

4. REFERENCES

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